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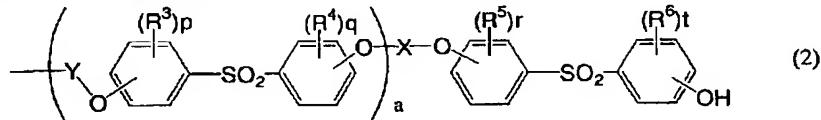
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(54)【発明の名称】ジフェニルスルホン化合物の製造方法

(57)【要約】

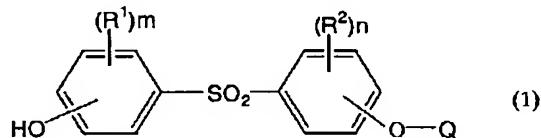
【課題】鉄分混入を極力防止することにより、着色がなく高純度なジフェニルスルホン化合物を工業的に有利に製造する。

【解決手段】鉄分含有量が0.05ppm以下の溶媒中で反応を行なう反応工程、若しくは鉄分含有量が0.05ppm以下の水を用いて化合物(1)を精製する精製工程を有する化合物(1)の製造方法、又は内壁に耐腐蝕性層を有する槽中で反応及び/若しくは精製を行うことを特徴とする化合物(1)の製造方法。



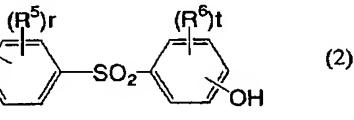
(X及びYは、エーテル結合を有してもよい炭化水素基等を表し、R³～R⁶はアルキル基等を表し、p、q、

【化1】



[R¹及びR²はアルキル基等を表し、m及びnは0～4の整数を表し、Qは水素原子、アルキル基又は式(2)]

【化2】

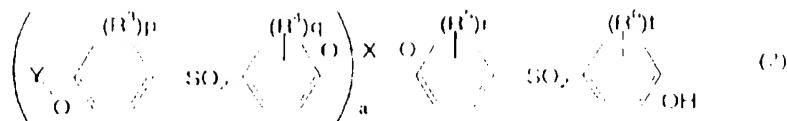
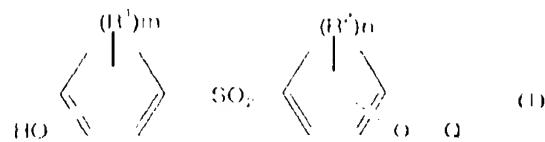


r、tは0～4の整数を表し、aは0～10の整数を表す。)で表される基等を表す。]

【物語】

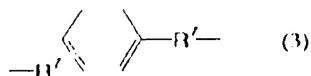
【化1】 (1) 前項 (1) に、置換基を有する。

【化2】



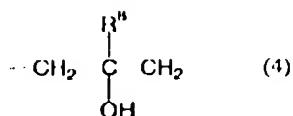
(式中、X及びYは、それぞれ独立して、置換基を有するC1～C12の飽和若しくは不飽和の炭化水素基、エーテル結合を有するC1～C12の飽和若しくは不飽和の炭化水素基、式(3))

【化3】

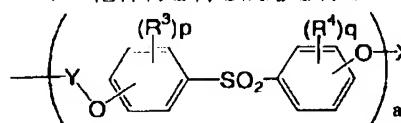


(式中、R'はC1～C4アルキル基又はC1～C4アルキル基を表す。)で表される基、又は式(4))

【化4】

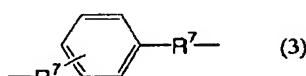


(式中、R^bは、水素原子又はC1～C4アルキル基を表す。)で表される基を表す。R¹～R⁶は、それぞれ独立して、ハロゲン原子、C1～C8アルキル基又はC2～C8アルケニル基を表し、p、q、r及びtは、それぞれ独立して、O又は1～4の整数を表し、aは0又は1～10の整数を表す。]で表される基を表す。上で表されるジフェニルスルホン化合物を得る反応を行なう



(式中、X及びYは、それぞれ独立して、置換基を有してもよいC1～C12の飽和若しくは不飽和の炭化水素基、エーテル結合を有するC1～C12の飽和若しくは不飽和の炭化水素基、式(3))

【化7】



(式中、R⁷は、メチレン基又はエチレン基を表す。)で表される基、又は式(4))

【化8】

(式中、R¹及OR²は、それぞれ独立して、ハロゲン原子、C1～C8アルキル基又はC2～C8アルケニル基を表す。)で表される基、又は式(1)で表されるジフェニルスルホン化合物の混合物から、式(1)で表されるジフェニルスルホン化合物以外の化

【化9】

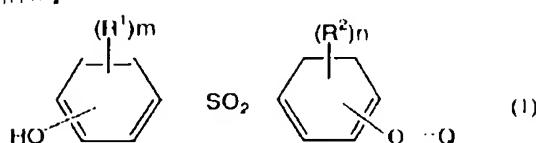


20 反応工程を行なう式(1)～(3)における各化合物の製造方法は、前記各項(1)～(3)の説明に有するO～Oのペリベンゼン上の着媒を用い、式(1)を特徴とする式(1)～(3)の各化合物の製造方法。

【請求項2】前記着媒(1)～(3)を含む反応着媒を用いることを特徴とする請求項1に記載の式(1)～(3)が示されるジフェニルスルホン化合物の製造方法。

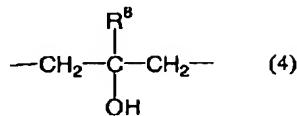
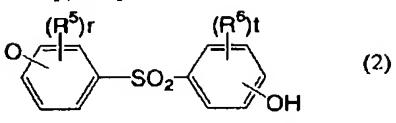
【請求項3】式(1)

【化5】



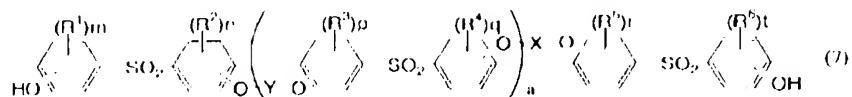
(式中、R¹及OR²は、それぞれ独立して、ハロゲン原子、C1～C8アルキル基又はC2～C8アルケニル基を表し、m及OR²は、それぞれ独立してO又は1～4の整数を表す。Qは、C1～C8アルキル基、C2～C8アルケニル基、C3～C8のシクロアルキル基、置換基を有してもよいアルキル基、又は式(2))

【化6】



(式中、R⁸は、水素原子又はC1～C4アルキル基を表す。)で表される基を表す。R³～R⁶は、それぞれ独立して、ハロゲン原子、C1～C8アルキル基又はC2～C8アルケニル基を表し、p、q、r及びtは、それぞれ独立して、O又は1～4の整数を表し、aは0又は1～10の整数を表す。]で表される基を表す。}で表されるジフェニルスルホン化合物を含む混合物から、式(1)で表されるジフェニルスルホン化合物以外の化

第二章：项目管理。主要讲解项目管理的基本概念、项目管理的流程、项目管理的工具和方法，以及项目管理中的常见问题和解决策略。



(式中、 R^+ = R'' 、 m 、 n 、 p 、 q 、 t 、 u 、 a 、 X 及 OY は、前記の同じ意味を有す。) 本表各化合物の構造式を第 1-6 の式、重ね方を記載の如く示す。但し、化合物の製品名を示す。

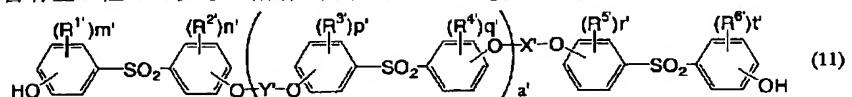
【請求項9】前記（1）～（9）のいずれかの化合物が、A₁、A₂、A₃、ジヒドロA₁、ジヒドロA₂、A₄、式（6）：R¹—A¹（式中、R¹は前記同じ意味を有し、A¹はハロゲン原子を表す。）で表される化合物上を、塩基存在下に反応させて得られる化合物である請求項1、6のいずれかに記載のジノニルスルホン化合物の製造方法。

【請求項10】前記式(1)で表されるジフェニルスルホン化合物が、4, 4'-ジヒドロキシジフェニルスルホン又は2, 4'-ジヒドロキシジフェニルスルホンと、式(8)： $\text{A}^2 - \text{X} - \text{A}^3$ 及び式(9)： $\text{A}^4 - \text{Y} - \text{A}^5$ (式中、 $\text{A}^2 \sim \text{A}^5$ は、それぞれ独立して、ハロゲン原子を表し、X及びYは、前記と同じ意味を表す。)で表される化合物とを、塩基存在下に反応させて得られる化合物である請求項1～6のいずれかに記載のジフェニルスルホン化合物の製造方法。

【発明の詳細な説明】

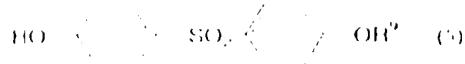
[0 0 0 1]

【発明の属する技術分野】本発明は、感熱記録剤の顕色剤及びその原料等として有用なジフェニルスルホン化合物を高純度かつ工業的に有利に製造する方法に関する。より詳しくは、反応工程若しくは精製工程で用いる溶媒(水)として、鉄分含有量が極めて少ない溶媒(水)を



For example, if $\{x_1, x_2, \dots, x_n\} = \{1, 2, \dots, n\}$, then $\{x_1^2, x_2^2, \dots, x_n^2\} = \{1^2, 2^2, \dots, n^2\} = \{1, 4, \dots, n^2\}$.

100



其中， $\Omega = \{1, 2, \dots, n\}$ 表示所有可能的事件空间， $\mathcal{A} = \{\emptyset, \Omega, A_1, A_2, \dots, A_m\}$ 表示一个事件的集合， $A_i \in \mathcal{A}$ 表示第 i 个事件， $P(A_i) = p_i$ 表示事件 A_i 的概率。

[[Table 3](#)] indicates that the H_2O_2 concentration in the aqueous phase is about 10 times higher than that in the organic phase.

Introduction

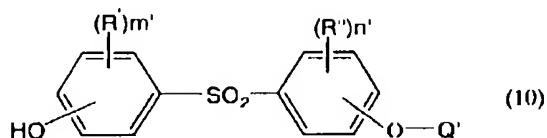
用いる。また上り、及び、又曰反応槽若しく曰精製槽にて、内壁に耐腐蝕性層を有する槽を用いる。また上り、重金属性等の混入を極力防止し、着色のない高純度等を、又は、ガスガラス化合物を製造する方法に関する。

[0002]

【保守の技術】式(10)

〔 〇〇〇 〕

[1 : 1 9]



【0004】(式中、R'、R''及びQ'はアルキル基等を表し、m'及びn'は0又は1~4の整数を表す。)で表される化合物(以下、「ジノエニルスルホン化合物」という。)は、顔色剤及びその他の製造原料等として有用である。

【0005】従来、4-置換ヒドロキシ-4'-ヒドロキシジフェニルスルホンの製造方法としては、例えば、4, 4'-ジヒドロキシジフェニルスルホンとアルキルハライド等のハログン化合物とを、アルカリの存在下に反応させる方法が知られている（特開平6-251248号公報、特開平5-255234号公報、特許公報第2500532号等参照）。また、式(1.1)

[0006]

【化201】

【0007】で表される化合物の製造方法としては、
4, 4' -ジヒドロキシジフェニルスルホン又は2,
4' -ジヒドロキシジフェニルスルホンと、一般式：A
 $A^2 - X' - A^3$ 及び一般式：A' - Y' - A⁵
(式中、A² ~ A⁵ は、それぞれ独立して、ハログン原子を表し、X' 及びY' は、前記と同じ意味を表す。) で表される化合物と、アルカリ存在下に反応させる方法が知られている(特開平10-29969号公报参照)。

【0008】しかしながら、ジフェニルスルホン化合物を上記のいずれかの方法により工業的規模で製造する場合には、反応液が着色し、それが目的物であるジフェニルスルホン化合物(結晶中)に取り込まれ、その後精製を繰り返しても完全に脱色することが困難な場合があった。

【0009】かかる場合には、反応混合物の液に活性炭を添加等して脱色する作業を行なっていた。しかしながら、活性炭を添加する方法ではある程度脱色することができるものの完全に脱色することが困難であり、また、添加した活性炭を濾別しなければならず、作業が煩雑となっていた。

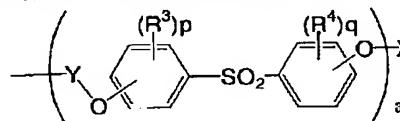
【0010】ジフェニルスルホン化合物は、主に顕色剤として用いられる。出発原料に着色物質が不純物として含まれていると、それがそのまま最終製品にも取り込まれ、最終製品も着色してしまうことになる。特にこれらの化合物は顕色剤として用いられるため、僅かな着色があっても問題となる。したがって、着色がなく高純度なジフェニルスルホン化合物を工業的に有利に製造する方法を確立することが必要とされていた。

【0011】

【発明が解決しようとする課題】本発明は、かかる実状に鑑みてなされたものであり、着色がなく高純度なジフェニルスルホン化合物を工業的に有利に製造する方法を提供することを課題とする。

【0012】

【課題を解決するための手段】本発明者らは、上記課題を解決すべく、ジフェニルスルホン化合物の製造工程において、反応混合物が着色する原因を詳細に調べた。そ



の結果、反応工程及び／又は精製工程において、槽(反応槽又は精製槽)から溶出し、又は溶媒として用いられる工業用水中に含まれる鉄分等の重金属イオンがジフェニルスルホン化合物等と反応して着色性の金属錯体を形成し、これが着色の原因物質であると考えられた。

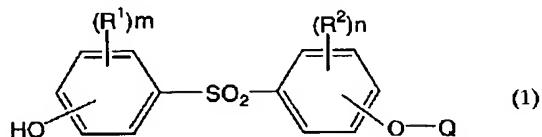
【0013】従来、ジフェニルスルホン化合物を反応させたり、反応混合物を精製する場合においては、反応溶媒又は精製溶媒として重金属イオンを比較的多く含む工業用水を用いていた。また、反応槽や精製槽として汎用性の高いSUS製の槽を用いていたため、強酸や強アルカリによって槽の内壁面が腐蝕される場合があり、鉄分等の重金属イオンが反応液に混入し易いものとなっていた。

【0014】そこで、反応工程又は精製工程において、鉄分含有量が0.05 ppm以下の溶媒を用い、及び／又は内壁に耐腐蝕性層を有する槽を使用して重金属イオンの混入を極力防止することにより、ジフェニルスルホン化合物の着色を効果的に防止できることを見出し、本発明を完成するに至った。

【0015】かくして本発明の第1によれば、溶媒中で、式(1)

【0016】

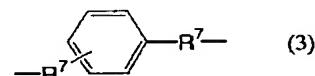
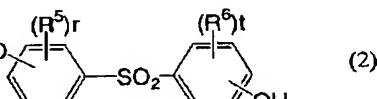
【化21】



【0017】(式中、R¹ 及びR² は、それぞれ独立して、ハログン原子、C1~C8アルキル基又はC2~C8アルケニル基を表し、m及びnは、それぞれ独立して0又は1~4の整数を表す。Qは、C1~C8アルキル基、C2~C8アルケニル基、C3~C8のシクロアルキル基、置換基を有してもよいアラルキル基、又は式(2)

【0018】

【化22】



【0021】(式中、R⁷ は、メチレン基又はエチレン基を表す。) で表される基、又は式(4)

【0022】

【化24】

ぞれ独立して、0又は1～4の整数を表す。

【0038】Qは、メチル基、エチル基、n-プロピル基、イソプロピル基、n-ブチル基、t-ブチル基等のC1～C8アルキル基；ビニル基、プロペニル基、イソプロペニル基、ブテニル基等のC2～C8アルケニル基；シクロプロピル基、シクロペンチル基、シクロヘキシル基等のC3～C8のシクロアルキル基；ベンジル基、4-クロロベンジル基、2-フェニルエチル基等の置換基を有してもよいアラルキル基；又は前記式(2)で表される基；を表す。

【0039】式(2)中、p、q、r及びtは、それぞれ独立して、0又は1～4の整数を表し、aは1～10の整数を表す。X及びYは、それぞれ独立して、メチレン基、エチレン基、トリメチレン基、テトラメチレン基、ペンタメチレン基、ヘキサメチレン基、ヘプタメチレン基、オクタメチレン基、ノナメチレン基、デカメチレン基、ウンデカメチレン基、ドデカメチレン基、メチルメチレン基、ジメチルメチレン基、メチルエチレン基、メチレンエチレン基、エチルエチレン基、1,2-ジメチルエチレン基、1-メチルトリメチレン基、1-メチルテトラメチレン基、1,3-ジメチルトリメチレン基、1-エチル-4-メチルテトラメチレン基、

【0040】2-ヒドロキシトリメチレン基、2-ヒドロキシ-2-メチルトリメチレン基、2-ヒドロキシ-2-エチルトリメチレン基、2-ヒドロキシ-2-プロピルトリメチレン基、2-ヒドロキシ-2-ブチルトリメチレン基等の置換基を有してもよいC1～C12の飽和炭化水素基；ビニレン基、プロペニレン基、2-ブテニレン基、エチニレン基、2-ブチニレン基、1-ビニルエチレン基等の置換基を有してもよいC1～C12の不飽和炭化水素基；エチレンオキシエチレン基、テトラメチレンオキシテトラメチレン基、エチレンオキシエチレンオキシエチレン基、エチレンオキシメチレンオキシエチレン基、1,3-ジオキサン-5,5-ビスマチレン基等のエーテル結合を有するC1～C12の飽和若しくは不飽和炭化水素基；式(3)で表される基、又は式(4)で表される基のいずれかを表す。

【0041】式(3)中、R⁷はメチレン基又はエチレン基を表す。また、式(4)中、R⁸は、水素原子；メチル基、エチル基、n-プロピル基、イソプロピル基、n-ブチル基、t-ブチル基等のC1～C4アルキル基；を表す。

【0042】R³～R⁶は、それぞれ独立して、フッ素、塩素、臭素等のハロゲン原子；メチル基、エチル基、n-プロピル基、イソプロピル基、n-ブチル基、t-ブチル基等C1～C8アルキル基；ビニル基、プロペニル基、イソプロペニル基、ブテニル基等のC2～C8アルケニル基；を表す。

【0043】前記式(5)中、R⁹は、メチル基、エチ

ル基、n-プロピル基、イソプロピル基、n-ブチル基、t-ブチル基等のC1～C8アルキル基；エテニル基、プロペニル基、イソプロペニル基、ブテニル基等のC2～C8アルケニル基；シクロプロピル基、シクロペンチル基、シクロヘキシル基等のC3～C8シクロアルキル基；又はベンジル基、4-クロロベンジル基、2-フェニルエチル基等の置換基を有してもよいアラルキル基を表す。

【0044】式(5)で表される化合物の具体例としては、4-メトキシ-4'-ヒドロキシジフェニルスルホン、4-エトキシ-4'-ヒドロキシジフェニルスルホン、4-n-ブロポキシ-4'-ヒドロキシジフェニルスルホン、4-イソプロロポキシ-4'-ヒドロキシジフェニルスルホン、4-n-ブトキシ-4'-ヒドロキシジフェニルスルホン、4-sec-ブトキシ-4-ヒドロキシジフェニルスルホン、4-t-ブトキシ-4'-ヒドロキシジフェニルスルホン等が挙げられる。

【0045】式(7)で表される化合物としては、例えば、以下のものが挙げられる。

1) X及び/又はYが置換基を有してもよいC1～C12の飽和炭化水素基である化合物；4-[4-(4-ヒドロキシフェニルスルホニル)フェノキシ-4-ブチルオキシ]-4'-[4-(4-ヒドロキシフェニルスルホニル)フェノキシ-3-プロピルオキシ]ジフェニルスルホン、4,4'-ビス[4-(4-ヒドロキシフェニルスルホニル)フェノキシ-2-エチルオキシ]ジフェニルスルホン、4,4'-ビス[4-(4-ヒドロキシフェニルスルホニル)フェノキシ-3-プロピルオキシ]ジフェニルスルホン、4,4'-ビス[4-(4-ヒドロキシフェニルスルホニル)フェノキシ-4-ブチルオキシ]ジフェニルスルホン、4,4'-ビス[4-(4-ヒドロキシフェニルスルホニル)フェノキシ-5-ペニチルオキシ]ジフェニルスルホン、4,4'-ビス[4-(4-ヒドロキシフェニルスルホニル)フェノキシ-6-ヘキシルオキシ]ジフェニルスルホン、4-[4-(4-ヒドロキシフェニルスルホニル)フェノキシ-4-ブチルオキシ]-4'-[4-(4-ヒドロキシフェニルスルホニル)フェノキシ-2-エチルオキシ]ジフェニルスルホン、4-[4-(4-ヒドロキシフェニルスルホニル)フェノキシ-3-プロピルオキシ]-4'-[4-(4-ヒドロキシフェニルスルホニル)フェノキシ-2-エチルオキシ]ジフェニルスルホン、4,4'-ビス[4-[4-(2-ヒドロキシフェニルスルホニル)フェノキシ]ブチルオキシ]ジフェニルスルホン、4,4'-ビス[4-(4-ヒドロキシフェニルスルホニル)フェノキシ]ブチルオキシ]ジフェニルスルホン、1,1-ビス[4-(4-ヒドロキシフェニルスルホニル)フェノキシ]メタン、1,2-ビス[4-(4-ヒドロキシフェニルスルホニル)フェノキシ]エタン、50 1,3-ビス[4-(4-ヒドロキシフェニルスルホニ

【0051】これらの化合物の中でも、本発明は、4-イソプロポキシ-4'-ヒドロキシジフェニルスルホン、又は式(7)中、aが0又は1~3の整数であり、X及び/又はYが、 $-CH_2-CH_2-O-CH_2-CH_2-$ 又は $-CH_2-CH=CHCH_2-$ である化合物を製造する場合に好ましく適用することができる。

【0052】前記式(1)で表されるジフェニルスルホン化合物は、(i)所定の原料を所定の条件下に反応させて、目的とするジフェニルスルホン化合物を含む反応混合物を得る反応工程と、(ii)該反応混合物から目的とするジフェニルスルホン化合物を単離する精製工程からなる製造方法によって製造することができる。

【0053】本発明は、前記式(1)で表されるジフェニルスルホン化合物の製造において、鉄分含有量が0.05 ppm以下の溶媒を用いることを第1の特徴とする。本発明において鉄分含有量とは、用いられる溶媒に含まれる鉄、鉄化合物及び鉄イオン(鉄原子を含むイオンを含む)等の鉄分であって、溶媒中に存在する形態で、又は酸若しくはアルカリと反応して鉄イオン又は鉄原子を含むイオンとなって、ジフェニルスルホン化合物と錯体を形成して着色物質となり得る物質のトータルの含有量をいう。

【0054】鉄分含有量が0.05 ppm以下の溶媒を得る方法としては、例えば、蒸留する方法や、イオン交換樹脂等の鉄分を捕獲する機能を持つ物質を充填したカラムの中に通す方法等の公知の方法が挙げられる。溶媒中に含まれる鉄分含有量は、例えば、紫外線又は可視分光光度計、誘導結合高周波プラズマ発光分光分析装置、原子吸光分析装置、光電光度計及び比色計等の測定装置によって測定することができる。

【0055】本発明は、内壁に耐腐蝕性層を有する反応槽又は精製槽(以下、これらを「槽」ともいう。)を用いることを第2の特徴とする。耐腐蝕性層の材料としては、反応工程又は精製工程において用いられる硫酸等の酸や水酸化ナトリウム等のアルカリに対し腐食されない性質を有するものであれば特に制限はない。

【0056】かかる耐腐蝕性材料としては、例えば、チタン、ジルコニアム、タンタル、ニオブ、ニッケル等の耐腐蝕性金属;ほうけい酸ガラス、中性ガラス、石英ガラス、耐アルカリガラス等のガラス、ほうろう等の無機材料;四フッ化エチレン樹脂(PTFE又はTFE)、四フッ化エチレン-パーコロアルコキシビニルエーテル共重合体(PFA)、四フッ化エチレン-六フッ化プロピレン共重合体(FEP)、ポリクロロトリフルオロエチレン(PCTFE)、四フッ化エチレン-エチレン共重合体(ETFE)、クロロトリフルオロエチレン-エチレン共重合体(ECTFE)、ポリビニリデンフ

ロライド(PVDF)、ポリビニルフロライド(PVF)等のフッ素樹脂等の有機材料;等が挙げられる。これらの中でも、入手が容易であること及び優れた耐腐食性を有すること等の観点から、チタン、ガラス及びフッ素樹脂からなる群から選ばれる少なくとも1種が好ましい。

【0057】耐腐食性層を内壁に形成する方法としては、例えば、内壁に耐腐食性材料をライニング又はコーティングする方法が挙げられる。ライニングあるいはコーティングする方法としては、例えば、ガラスを用いる場合には、槽を構成する基材(鋼板)表面にガラス質の釉を焼き付けるガラスライニングが挙げられる。また、フッ素樹脂を用いる場合には、例えば、粉体焼き付けによるコーティングやガラスクロスを用いるシートライニング等が挙げられる。これらの中でも、耐熱性、耐久性等の観点から、ガラス又はフッ素樹脂を槽の内壁にライニング又はコーティングした槽の使用が好ましく、ガラスを槽の内壁にライニングした槽(通称:GL)の使用がより好ましい。

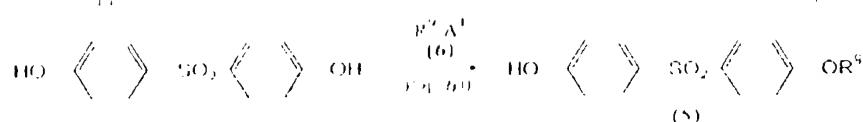
【0058】本発明においては、(a)鉄分含有量が0.05 ppm以下の溶媒、好ましくは鉄分含有量が0.05 ppm以下の(水を含む反応溶媒及び/又は精製水)を用い、従来通りSUS製の槽中で行う方法、(b)従来通りの溶媒を用い、内壁に耐腐蝕性層を有する槽中で反応又は精製を行う方法、又は(c)鉄分含有量が0.05 ppm以下の溶媒、好ましくは鉄分含有量が0.05 ppm以下の(水を含む反応溶媒及び/又は精製水)を用い、かつ、内壁に耐腐蝕性層を有する槽を使用する方法のいずれかであってよいが、より確実に着色のない高純度なジフェニルスルホン化合物を得ることができる観点から、(c)の方法が特に好ましい。

【0059】以下、本発明の製造方法を得られるジフェニルスルホン化合物の種類に分けて説明する。以下の説明においては、反応溶媒及び精製水として、鉄分含有量が0.05 ppm以下の反応溶媒及び精製水を使用し、かつ、内壁に耐腐蝕性層を有する槽を使用している。

【0060】(I)式(5)で表される4-置換ヒドロキシ-4'-ヒドロキシジフェニルスルホンの製造
前記式(5)で表される化合物(以下、「化合物(5)」)というは、4,4'-ジヒドロキシジフェニルスルホンと式(6): R^9-A' で表される化合物(以下、「化合物(6)」)とを、溶媒中、塩基存在下に反応させることで得ることができる(下記反応式参照)。

【0061】

【化27】

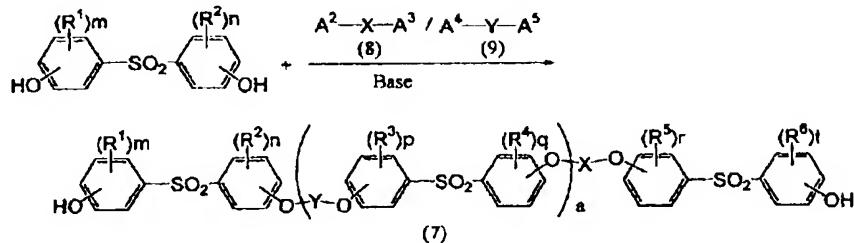


【006】中：P=1mmol/L的浓度下，X
的吸收峰强度比对照组低约30%。在
此浓度下，抑制率为30%左右。因此，
本品对胰岛素的降血糖作用有抑制作用。
1.4.4 对胰岛素的抑制作用
本品抑制胰岛素的降血糖作用，抑制
率为30%左右。

【0064】用いる溶媒は上(1)、例(1)、本、又日本
トール油、本-A-1等、本-A-1等の其相を混
合溶媒等が好ましい。本又日本トール油の混合溶
媒の使用が好ましい。溶媒の使用量は、(4)、(4')、(4)
トロリシジンノルマル水(1 g)に対してC、油常、O、
1~1.0 m²の範囲である。反応は、油常、室温、溶媒
の沸点、好ましく4.5~6.5°Cの温度範囲で行われ、
通常、20~25時間で終了する。

【0065】この反応においては、反応が完全に進行せず副反応も進行することから、通常、反応混合物には目的物の他に、未反応の化合物（6）や未反応の4, 4'-ジヒドロキシジフェニルスルホン、副生成物である4, 4'-ジ置換ヒドロキシジフェニルスルホン等の不純物が含まれている。

【0066】未反応の化合物(6)を除去する方法としては、例えば、反応終了後、反応液を加熱して化合物(6)を蒸発留去させる方法が挙げられる。また、化合



【0072】(式中、 $R^1 \sim R^6$ 、 $A^2 \sim A^5$ 、 a 、 m 、 n 、 p 、 q 、 r 、 t 、 X 及び Y は、前記と同じ意味を表す。)

出発原料としては、入手容易性及び汎用性の観点から、
4, 4' -ジヒドロキシジフェニルスルホン若しくはそ
の誘導体又は2, 4' -ジヒドロキシジフェニルスルホ

从以上分析中可以看出，影响因素有：①土壤的物理性质；②土壤的化学性质；③土壤的生物活性；④土壤的微生物种类和数量；⑤土壤的微生物活性；⑥土壤的微生物多样性。

【0.06%】： Na_2HPO_4 調整，使之呈弱酸性，並
加 CaCO_3 之量，使之成中性時，即為最適量。
（二）例：以 FeCl_3 作水垢抑制劑者，當加入 FeCl_3 時，
水垢之水垢側之 pH 值，水垢側 pH 值在所定之值上調整之，其目的半半價化合物（3）在有水垢側——4.
47，而 Fe(OH)_3 在水垢側之水垢側一分離，
水垢之水垢側在某點上，即為

【0068】反応混合物のpH値の調整(1)、例(1)、反応混合物に硫酸、硝酸、塩酸等の酸又は本酸性、ナトリウム、本酸性カリウム等のアルカリ水溶液を揮発しない少量ずつ添加する事により有効である。pH値の調整(1)、例(1)が正確に行なう必要がある。また、アルカリ可溶性の副生成物と目的物との分離を確実に達成するため、pH値の設定値を変化させり抽出する操作を複数回繰り返して行なう事もできる。

【0069】次いで、得られた有機層を冷却して晶析させり、析出結晶をろ取し、水洗及び乾燥する。古に上り、着色のない4-置換ヒドロキシ-4'-ヒドロキシジフェニルスルホンを高純度かつ収率よく得る事ができる。

【0070】(11)式(7)で表される化合物の製造
 式(7)で表される化合物(以下、「化合物(7)」といふ。)は、例えば、特開平10-29969号公報の記載の方法に準じて製造することができる。具体的には、次の反応式で示される方法で行うことができる。

100711

【化28】

ン若しくはその誘導体が好ましい。

【0073】式(8)及び式(9)中、 $A^2 \sim A^5$ は、それぞれ独立して、フッ素、塩素、臭素、ヨウ素等のハロゲン原子を表す。これらの中でも、 A^2 と A^3 、及び A^4 と A^5 の間で反応性に差をもたせて、反応を制御できる観点から、 A^2 と A^3 、及び A^4 と A^5 は、例えば

塩素原子と臭素原子等のように異なるハロゲン原子であるのが好ましい。

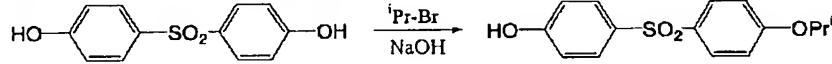
【0074】反応は、塩基の存在下、水、極性有機溶媒又は水-非水混和性有機溶媒の二層系のいずれかで行うのが好ましい。水混和性有機溶媒としては、例えば、N, N-ジメチルホルムアミド、N, N-ジメチルアセタミド、1, 3-ジメチルイミダゾリジン、1, 3-ジメチル-2-イミダゾリジノン、N-メチルピロリドン、ヘキサメチルリン酸トリアミド等のアミド系溶媒；テトラヒドロフラン；アセトン；ジメチルスルホキシド；等が挙げられる。

【0075】また、非水混和性有機溶媒としては、例えば、ベンゼン、トルエン、クロロベンゼン、ジクロロベンゼン等の芳香族炭化水素系溶媒；ジエチルケトン、メチルイソブチルケトン(MIBK)、シクロヘキサン等のケトン系溶媒；酢酸エチル、酢酸プロピル等のエスチル系溶媒；ジエチルエーテル、ジイソプロピルエーテル等のエーテル系溶媒；等が挙げられる。

【0076】これらの中でも、収率よく目的物が得られること等から、アセトン、メチルイソブチルケトン等のケトン系溶媒；N, N-ジメチルホルムアミド、N, N-アセタミド等のアミド系溶媒；テトラヒドロフラン；等の水混和性又は非水混和性極性有機溶媒の使用が好ましい。

【0077】用いる塩基としては、例えば、水酸化ナトリウム、水酸化カリウム等のアルカリ金属水酸化物；水酸化マグネシウム、水酸化カルシウム等のアルカリ土類金属水酸化物；炭酸ナトリウム、炭酸カリウム等のアルカリ金属炭酸塩；炭酸マグネシウム、炭酸カルシウム等のアルカリ土類金属炭酸塩；が挙げられる。これらの中でも、水酸化ナトリウム等のアルカリ金属水酸化物の使用が好ましい。反応温度は、通常-20℃から150℃、好ましくは30℃から120℃の範囲であり、反応時間は、通常、数時間から十数時間である。

【0078】反応混合物の精製方法は、不純物を除去できる方法であれば特に制限はないが、pH調整により化合物(7)と不純物とを分離する方法が簡便である。例えば、反応混合物に水又は水-アルコール溶媒を添加し



【0085】4, 4'-ジヒドロキシジフェニルスルボン450g、4.8%水酸化ナトリウム水溶液255ml及び蒸留水120mlをGL槽に仕込み、攪拌しながら75℃に昇温させて全容を均一な溶液とした。得られた溶液に、イソプロピルプロマイド225gを55±3℃でゆっくりと滴下し、滴下終了後さらに55±5℃で攪拌を継続した。滴下開始からトータルで20時間経過後、反応液に80℃の蒸留水235mlを加え、80℃で1時間加熱して、未反応のイソプロピルプロマイドを蒸発留去させた。その後、80℃の蒸留水300ml及

た後、反応混合物を所定のpH値に調整し、冷却することにより溶解度の差を利用して化合物(7)を優先的に析出させる方法が挙げられる。

【0079】用いるアルコールとしては、例えば、メタノール、エタノール、プロパノール等の低級アルコールが挙げられる。水又は水-アルコール溶媒の使用量は、反応混合物に対して、1~5倍重量部である。

【0080】反応混合物のpH値の調整は、例えば、反応混合物に硫酸、硝酸、塩酸等の酸又は水酸化ナトリウム、水酸化カリウム等のアルカリ水溶液を、攪拌下に少量ずつ添加することにより行われる。pH値の調整は均一かつ正確に行う必要がある。また、分離を確実に達成するために、pH値の設定値を変化させて抽出する操作を複数回繰り返して行うこともできる。最後に、析出結晶をろ取し、水又は水-アルコール溶媒で洗浄、乾燥することにより、着色のない化合物(7)を高純度かつ収率よく得ることができる。

【0081】

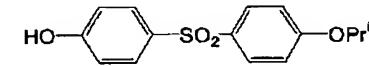
【実施例】以下、本発明を実施例により更に詳細に説明する。本発明は下記の実施例に限定されることなく、本発明の主旨を逸脱しない範囲で、ジフェニルスルボン化合物の種類、反応及び精製工程において用いる槽の種類等を自由に変更することができる。

【0082】なお、実施例においては全て蒸留水を用い、比較例においては全て工業用水を使用した。用いた蒸留水及び工業用水について鉄分含有量を、誘導結合高周波プラズマ発光分光分析装置により測定したところ、蒸留水の鉄分含有量は0.05ppm以下であり、工業用水の鉄分含有量は0.26ppmであった。また、実施例においては、反応槽及び精製槽として、内壁をガラスライニングした槽(以下、「GL槽」という。)を用い、比較例においては、一般的に用いられているSUS製の槽を用いた。

【0083】(実施例1) 4-イソプロポキシ-4'-(ヒドロキシジフェニルスルボンの製造

【0084】

【化29】

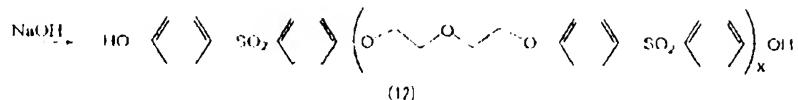
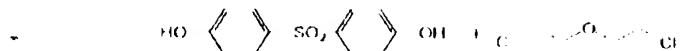


びトルエン250mlを80℃で加えて十分に攪拌し、水層を分取した。

【0086】次いで、水層にトルエン1100ml及び蒸留水200mlを79℃で加え、同温度で30分間攪拌した。さらに、30%希硫酸を攪拌しながら82℃で少量ずつ1時間かけて滴下して、反応液が均一にpH8.3~8.7になるように調整した。このものを82℃で30分間静置した後、トルエン層を分取した。さらに、このトルエン層にトルエン250ml及び水250mlを82℃で加え、同温度で2時間攪拌した後、82

C = 3.0% 时的 η_{eff} 为 0.0015，而当 C = 0.5% 时的 η_{eff} 为 0.0005。因此，当 C = 3.0% 时的 η_{eff} 是 C = 0.5% 时的 η_{eff} 的三倍。这说明，当 C = 3.0% 时，溶液中存在大量的聚丙烯酸钠，从而抑制了聚丙烯酸钠的溶解度，使聚丙烯酸钠的溶解度降低，从而导致 η_{eff} 增大。

【例 1】(1) 例 1) $\lim_{n \rightarrow \infty} \frac{1}{n^2}$ 不存在。
 (2) $\lim_{n \rightarrow \infty} (-1)^n$ 不存在。



【00090】 (式中、 x は 1 ～ 10 の整数を表す。)
 G.L.槽中に、蒸留水 4.7, 5 mℓ、氷酸化ナトリウム 2.5, 6 g, 4, 4'-(1,4-DA)、(1)、カルボルホルム 8.0, 0.8 g を加え、110 ± 2°C で 4 時間攪拌して溶解し、0.7, 7.7, 7.7 g (2, クロロメチル) チオカルボルム 3.4 g を 110 ～ 112°C で加え、同温度で 8 時間攪拌した。反応終了後、反応液に熱水 1.08, 1 mℓ を加え (80°C 上で冷却し、9.0% メタノール水溶液 1.67, 4 mℓ を 70°C で加え (均一な溶解となるように 30 分間攪拌した)。次いで、7.1°C で 1.0% 氷酸ナトリウム 1.6, 4 g をゆっくりと滴下し (pH を 4 ～ 5 とした)。7.1°C で 1 時間放置した後、2.5 ～ 3.0°C で冷却し、さらに 8 時間放置した。析出結晶をろ取し、5.0% メタノール水溶液 20.0 mℓ で洗浄し、乾燥して目的物 (12) の粉末 6.3, 2 g を得た (収率 7.8%)。得られた化合物 (12) の純度は 9.9% 以上であった。また、このものを色差計 (日本測色工業 (株) 製、型式: 1001D)

Figure 1. The effect of the number of nodes on the performance of the proposed algorithm.

Journal

[{1, 3, 0}]

D) (侧光) $I_1 = 1$, $I_2 = 0$, $I_3 = 0$ (侧光), 着色

【例 9-1】(比較例 2) 有機物の前記化学式 (1) と (2) の構造。

G.L.槽に代り、G.U.D.製の槽を用い、蒸溜水に代り、工業用水を用いる以外は実施例2と同様にして、化合物(1-2)の粉末6.3 gを得(收率78%)。得られた化合物(1-2)の純度は9.8%以上である。上記の4の赤色差計(日本電色工業(株)製、型式:100-1DP)で測定したところ、E値は4.4であり、淡桃色の着色が見られる。

〔 0 0 9 2 〕

【発明の効果】以上説明したように、本発明によれば、従来の製造ラインに大幅に変更を加えることなく簡便に、着色のない高純度なジフェニルスルホン化合物を効率よく製造することができる。

Description**Technical Fields:**

5 [0001] The present invention relates to processes for the preparation of 4,4'-dihydroxydiphenyl sulfone monoethers, useful as developers for thermal recording agents.

Background Art

10 [0002] Dihydroxydiphenyl sulfone monoethers are developers excellent in coloring sensitivity, preservability, heat resistance and other properties, and are often used for thermal recording papers, for facsimiles, barcodes, receipts and the like.

15 [0003] Processes for the preparation of, for example, a 4 alkoxy 4' hydroxydiphenyl sulfone (which may hereinafter refer to as the target compound), among the dihydroxydiphenyl sulfone monoethers, by a reaction of 4,4'-dihydroxy diphenyl sulfone (which may hereinafter refer to as BPS) with a halogen compound such as an alkyl halide in the presence of an alkali in a polar solvent such as dimethylformamide, dimethyl sulfoxide and alcohol, have been disclosed in each of Japanese Patents Laid open Nos. Sho 58-20483, Sho 58-82788, Sho 60-13852, Sho 60-56949 and Hei 6-25148. These methods have a drawback that it is difficult to improve reaction selectivity because of use of solvents dissolving reaction reagents and reaction products very well. A problem has been a production of a noticeable amount of a diether derivative byproduct, 4,4'-dihydroxydiphenyl sulfone diether.

20 [0004] WO 91/11433 has disclosed that a reaction of BPS with an alkyl halide in the presence of 1.5 to 3 moles of an alkali to a mole of BPS in 0.3 to 1.5 parts by weight of an aqueous solvent to a part by weight of 4,4'-dihydroxydiphenyl sulfone gives satisfactory results in both selectivity and yield.

25 [0005] Japanese Patent Laid open No. Hei 3-258760 describes a method for separating BPS from a 4 alkoxy 4' hydroxydiphenyl sulfone, in which an aqueous alkali solution and alcohols or ketones that do not mix with water are added to mix with a mixture containing BPS and a 4 alkoxy 4' hydroxydiphenyl sulfone, and the 4 alkoxy 4' hydroxy diphenyl sulfone is moved into the organic layer and the alkali metal salt of BPS into the aqueous layer for separation.

30 [0006] In Japanese Patent Laid open No. Hei 60-56949, a purification method of a 4 alkoxy 4' hydroxydiphenyl sulfone is described in which a solution of a water nonmiscible organic solvent containing a 4 alkoxy 4'-hydroxydiphenyl sulfone and unreacted BPS that is produced when BPS is alkylated or by other methods is shaken with an aqueous solution of hydrogen carbonate so that BPS moves into water for removal.

35 [0007] Japanese Patent Laid open No. Hei 5-255234 describes a method for producing a 4-alkoxy-4'-hydroxydiphenyl sulfone, in which an alkyl halide is added to a two-phase solvent system consisting of an aqueous solution of an alkaline compound in which BPS is dissolved and a water-nonmiscible organic solvent, and an alkaline compound is added to keep pH to 7.5 to 9.5, in a method for producing a 4-alkoxy-4'-hydroxydiphenyl sulfone by reacting BPS with an alkyl halide.

40 [0008] Japanese Patent Laid-open No. Hei 10-158235 has disclosed a method for purifying a 4-alkoxy-4'-hydroxydiphenyl sulfone, in which an alkali metal ion donor is added to an aqueous solution of a mixture containing a BPS alkali metal salt and an alkali metal salt of a 4-alkoxy-4'-hydroxydiphenyl sulfone to deposit and separate the alkali metal salt of 4-alkoxy-4'-hydroxydiphenyl sulfone, followed by treatment of the salt with an acid.

45 [0009] In the above production methods, the reaction solution contains the target compound as well as unreacted BPS, a byproduct of 4,4'-dialkoxydiphenyl sulfone and other impurities, as a side reaction proceeds simultaneously. These impurities damage the performance of the product when used as a developer. Therefore, a purification process to remove the impurities from the reaction solution is required.

50 [0010] Of the said impurities, the 4,4'-dialkoxydiphenyl sulfone, which is insoluble in water, can be removed in a way that the reaction solution is made an aqueous alkaline solution, a water-nonmiscible organic solvent is added and the sulfone is extracted into the organic layer for separation.

55 [0011] To remove unreacted BPS, a water-nonmiscible organic solvent is added to the reaction solution to produce a two-phase system consisting of an organic and an aqueous layers, the pH value of the aqueous layer is adjusted to a preset value to move the target compound into the organic layer and BPS into the aqueous layer, then the organic layer is separated, washed with water if necessary and cooled, and deposited crystals are separated by filtration so as to give the target compound. This separation/purification method utilizes the difference in acidity between the phenolic hydroxyl groups of BPS and the target compound.

55 Disclosure of the Invention:

[0012] However, the difference in acidity between the phenolic hydroxyl groups of BPS and the target compound is subtle. BPS is completely removed if the pH of the aqueous layer is higher than the preset value. Then, it becomes

difficult to separate the target compound completely into the organic layer, resulting in a large loss of the target compound. On the contrary, if the pH of the aqueous layer is lower than the preset value, the loss of the target compound is small. There has been a problem however that BPS moves into the organic layer so as to mix into the target compound as an impurity.

5 [0013] As described above, 4,4'-dihydroxydiphenyl sulfone monoethers produced by methods of the prior art may not have been satisfactory in terms of purity. Particularly when a reaction solution obtained from a reaction of materials at high concentrations is purified according to the aforementioned methods, BPS often tends to mix into the target compound as an impurity because of insufficient purification.

10 [0014] 4,4-Dihydroxydiphenyl sulfone monoethers are mainly used as developers. There have however been problems that, for example, a so-called background foggy phenomenon, which is the coloring of the surrounding area of a heated part on a thermal recording paper, occurs if 0.4% or more of BPS is contained in 4,4'-dihydroxydiphenyl sulfone monoethers. Therefore, development of production methods for isolating highly pure 4,4'-dihydroxydiphenyl sulfone monoethers has been looked for.

15 [0015] When 4,4'-dihydroxydiphenyl sulfone monoethers are produced in industrial scales, reaction solutions may sometimes be colored. In this case, the products, 4,4'-dihydroxydiphenyl sulfone monoethers, are also colored. It is sometimes difficult to decolor the products (to remove coloring substances) completely, even if processes such as decoloring and purification using activated carbon and the like are carried out afterward. Another problem has been a requirement of a new process for removing the added decoloring agents.

20 [0016] As described above, 4,4'-dihydroxydiphenyl sulfone monoethers are mainly used as developers. Because of the purpose of their use, developers are not satisfactory even if slightly colored.

[0017] It has been required therefore to establish industrial processes for producing non-colored, highly pure 4,4'-dihydroxydiphenyl sulfone monoethers in high yield.

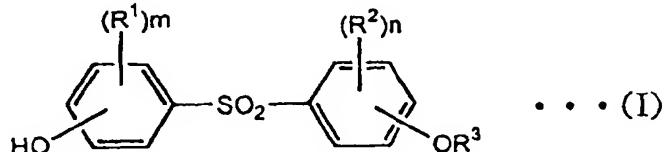
25 [0018] In addition, when 4,4'-dihydroxydiphenyl sulfone monoethers are taken out as crystals at the final stage and the crystals are dried by a hot dryer, the crystals may become lumps so that solvents cannot be removed completely. The monoethers containing solvents have a problem of performance as products. As 4,4'-dihydroxydiphenyl sulfone monoethers are used in the state of dispersing in solvents such as water, products of small crystal size, which are easily dispersed, are demanded. If there are block particles after the crystals are dried, a further process for pulverizing is required. To produce a product of small particle size, pulverization process work has sometimes become too complicated.

30 [0019] The present invention has been carried out in consideration of the aforementioned situations. It is an object of the present invention to provide methods for producing non-colored, highly pure 4,4'-dihydroxydiphenyl sulfone monoethers in high yield and advantageously in industrial production.

35 [0020] The inventors of the present invention have studied in earnest to solve the above problems. As a result, it has been found that the problems can be solved by that (1) BPS is removed efficiently if pH is adjusted step by step, (2) an alkyl halide used in the reaction remains and decomposes in the forming process so as to color the product, (3) the presence of metal ions, such as iron, in a solvent used in the production process causes coloring and substances producing the ions are removed, and (4) the product is dried with mechanical stir. Thus the present invention has been completed.

40 [0021] The present invention relates to

(Composition 1) a process for the preparation of a compound represented by Formula (I)



50 (wherein, R¹ and R² are each independently halogen, alkyl having 1 to 8 carbons or alkenyl having 2 to 8 carbons; m and n are each independently 0 or an integer of 1 to 4; and R³ is alkyl having 1 to 8 carbons, alkenyl having 2 to 8 carbons, cycloalkyl having 3 to 8 carbons or optionally substituted aralkyl), in which there are processes that an aqueous solution containing a compound of Formula (I) is adjusted pH to a preset value (P1), extracted with an organic solvent and separated to an organic and an aqueous layers, and that water or water adjusted to a fixed pH value is added to the separated organic layer in order to adjust the pH of the aqueous layer to a preset value (P2) for the separation of the organic layer;

55 (Composition 2) a process for the preparation of a compound of Formula (I) according to (Composition 1) in which the

process, that an aqueous solution containing a compound of Formula (I) is adjusted pH to a preset value (P1), extracted with an organic solvent and separated to an organic and an aqueous layers; in a process, that the aqueous layer of a two phase solution consisting of water and a water nonmiscible organic solvent with a mixture containing a compound of Formula (I) is adjusted pH to the preset value (P1) for separating the organic layer;

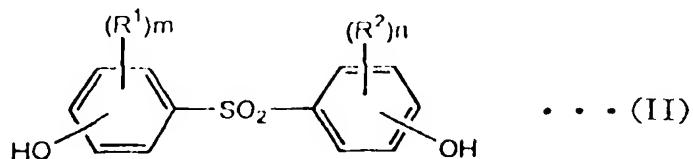
5 (Composition 3) a process for the preparation of a compound of Formula (I) according to (Composition 1) or (Composition 2) in which the said P2 is set to a value different from the said P1;

(Composition 4) a process for the preparation of a compound of Formula (I) according to one of (Composition 1) to (Composition 3) in which the said P2 is set to a value lower than the said P1;

10 (Composition 5) a process for the preparation of a compound of Formula (I) according to one of (Composition 1) to (Composition 4) in which the said P1 is set in a range of 8.4 and 8.7 and the said P2 between 8.3 and 8.6;

(Composition 6) a process for the preparation of a compound of Formula (I) according to one of (Composition 1) to (Composition 5) in which the aqueous solution containing a compound of Formula (I) is an aqueous solution containing the reaction product obtained from a reaction of a compound represented by Formula (II)

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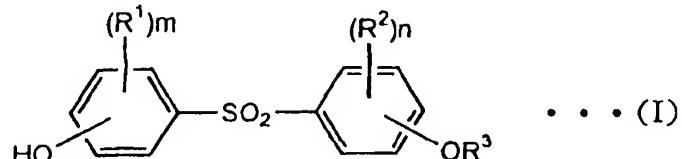
(wherein, R¹ and R² are each independently halogen, alkyl having 1 to 8 carbons or alkenyl having 2 to 8 carbons, m and n are each independently 0 or an integer of 1 and 4) with a compound of Formula (III)



30 (wherein, R³ is alkyl having 1 to 8 carbons, alkenyl having 2 to 8 carbons, cycloalkyl having 3 to 8 carbons or optionally substituted aralkyl, and X is halogen) in a solvent in the presence of a base;

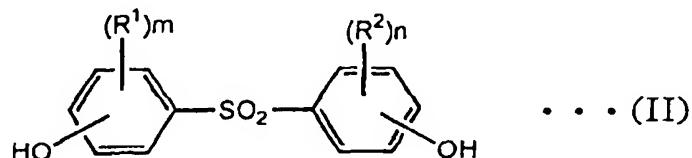
(Composition 7) a process for the preparation of a compound of Formula (I)

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(wherein, R¹ and R² are each independently halogen, alkyl having 1 to 8 carbons or alkenyl having 2 to 8 carbons; m and n are each independently 0 or an integer of 1 to 4; and R³ is alkyl having 1 to 8 carbons, alkenyl having 2 to 8 carbons, cycloalkyl having 3 to 8 carbons or optionally substituted aralkyl), characterized in that, in a method for producing a compound of Formula (I) by reacting a compound of Formula (II)

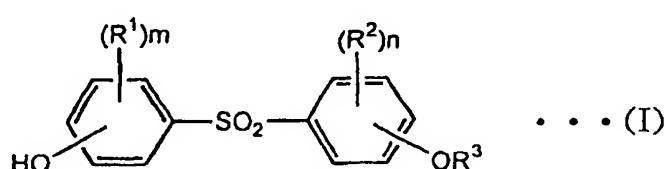
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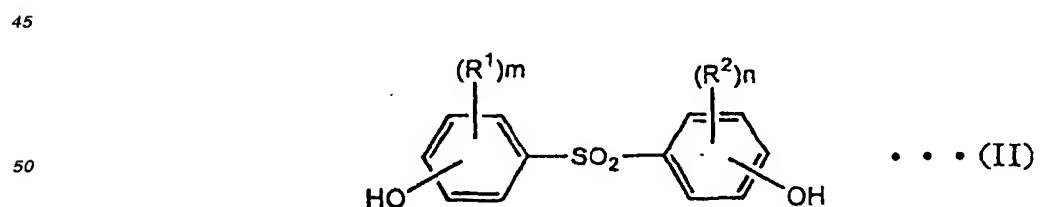
55 (wherein, R¹, R², m and n are as defined above) with a compound of Formula (III)



5 (wherein R³ is as defined above and X is halogen) in a solvent in the presence of a base and the obtained reaction
solution is purified, a process is provided that the compound of Formula (III) is removed from the solution produced by
the reaction of the compounds of Formulae (II) and (III);
(Composition 8) a process for the preparation of a compound of Formula (I) according to (Composition 7) in which the
said reaction solution is the reaction solution after the reaction of compounds of Formulae (II) and (III) is finished;
(Composition 9) a process for the preparation of a compound of Formula (I) according to (Composition 7) or (Compo-
10 sition 8) in which the process for removing the compound of Formula (III) from the reaction solution is provided imme-
diately after the compounds of Formulae (II) and (III) are reacted in a solvent in the presence of an alkali;
(Composition 10) a process for the preparation of a compound of Formula (I) according to one of (Composition 7) to
(Composition 9) in which a process for adjusting pH of solutions including the reaction solution is provided in the
15 production method of a compound of Formula (I), and the process for removing the compound of Formula (III) from
the reaction solution is provided immediately before the process for adjusting the pH of the solutions including the
reaction solution;
(Composition 11) a process for the preparation of a compound of Formula (I) according to one of (Composition 7) to
(Composition 10) in which the process for removing the compound of Formula (II) is a process for removing the com-
19 pound of Formula (III) together with the reaction solvent from the reaction solution by distillation;
(Composition 12) a process for the preparation of a compound of Formula (I) according to one of (Composition 7) to
(Composition 10) in which the process for removing the compound of Formula (III) is a process for removing the com-
20 pound together with a mixture of water and a solvent azeotropic with water by distillation;
(Composition 13) a process for the preparation of a compound of Formula (I) according to one of (Composition 7) to
(Composition 12) in which the reaction solvent is water;
25 (Composition 14) a process for the preparation of a compound of Formula (I) according to one of (Composition 7) to
(Composition 13) in which a process for depositing the compound of Formula (I) from an organic solvent as crystals
is provided in the production method of the compound of Formula (I), and the compound of Formula (III) is removed
so that the concentration of the compound in the organic solvent is 1% by weight or less;
30 (Composition 15) a process for the preparation of a compound of Formula (I)



40 (wherein, R¹ and R² are each independently halogen, alkyl having 1 to 8 carbons or alkenyl having 2 to 8 carbons; m
and n are each independently 0 or an integer of 1 to 4; and R³ is alkyl having 1 to 8 carbons, alkenyl having 2 to 8
carbons, cycloalkyl having 3 to 8 carbons or optionally substituted aralkyl), characterized in that, in a method for pro-
ducing a compound of Formula (I) by reacting a compound of Formula (II)



55 (wherein, R¹, R², m and n are as defined above) with a compound of Formula (III)

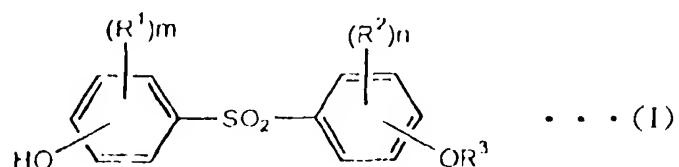


(wherein R^1 is as defined above and X is halogen) in a solvent in the presence of a base and the obtained reaction solution is purified, the compound of Formula (III) in the organic solvent is 6% by weight or less in concentration in the process; for purifying the reaction mixture of the compounds of Formulae (II) and (III) with water and an organic solvent (Composition 16) a process for the preparation of a compound of Formula (I) according to (Composition 15) in which the compound of Formula (III) in the organic solvent is 2% by weight or less in concentration;

(Composition 17) a process for the preparation of a compound of Formula (I) according to (Composition 15) in which the compound of Formula (III) in the organic solvent is 1% by weight or less in concentration;

(Composition 18) a process for the preparation of a compound of Formula (I)

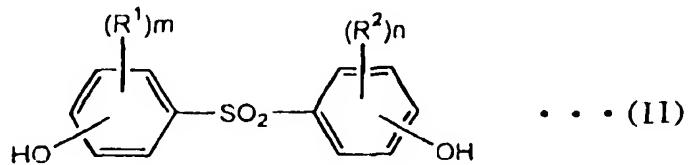
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(wherein, R^1 and R^2 are each independently halogen, alkyl having 1 to 8 carbons or alkenyl having 2 to 8 carbons, m and n are each independently 0 or an integer of 1 to 4, and R^1 is alkyl having 1 to 8 carbons, alkenyl having 2 to 8 carbons, cycloalkyl having 3 to 8 carbons or optionally substituted aralkyl), characterized in that, in a method for producing a compound of Formula (I) with a process for reacting a compound of Formula (II)

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(wherein, R^1 , R^2 , m and n are as defined above) with a compound of Formula (III)

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(wherein R^3 is as defined above and X is halogen) in the presence of 1.5 to 3 moles of an alkali to a mole of the compound of Formula (II) in 0.3 to 1.5 parts by weight of an aqueous solvent to a part by weight of the compound of Formula (II) and the compound of Formula (III) is removed by distillation, the compound of Formula (III) is heated to distill out and then water is further added to distill the compound of Formula (III) to remove;

(Composition 19) a process for the preparation of a compound of Formula (I) according to (Composition 18) in which an amount of water added is in the range of 0.03 and 0.1 parts by weight to a part by weight of the compound of Formula (II);

(Composition 20) a process for the preparation of a compound of Formula (I) according to (Composition 18) in which an amount of water added is in the range of 0.04 and 0.08 parts by weight to a part by weight of the compound of Formula (II);

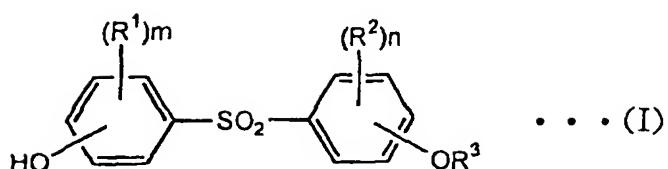
(Composition 21) a process for the preparation of a compound of Formula (I) according to (Composition 18) in which water is added separately over two or more times;

(Composition 22) a process for the preparation of a compound of Formula (I) according to (Composition 21) in which an amount of water added at the beginning is in the range of 0.03 and 0.1 parts by weight to a part by weight of the compound of Formula (II);

(Composition 23) a process for the preparation of a compound of Formula (I) according to (Composition 21) in which an amount of water added is between 0.04 and 0.08 parts by weight to a part by weight of the compound of Formula (II);

(Composition 24) a process for the preparation of a compound of Formula (I)

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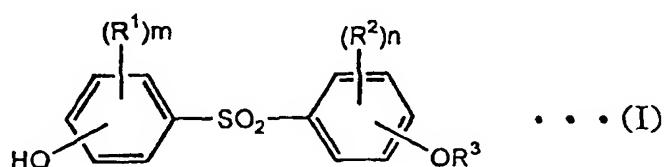
10 (wherein, R¹ and R² are each independently halogen, alkyl having 1 to 8 carbons or alkenyl having 2 to 8 carbons; m and n are each independently 0 or an integer of 1 to 4; and R³ is alkyl having 1 to 8 carbons, alkenyl having 2 to 8 carbons, cycloalkyl having 3 to 8 carbons or optionally substituted aralkyl), characterized in that, in a method for producing a compound of Formula (I) that a reaction is carried out in a solvent to give the compound of Formula (I), a solvent containing 0.05 ppm or less of iron components is used as the solvent;

15 (Composition 25) a process for the preparation of a compound of Formula (I) according to (Composition 24) in which the reaction solvent is a reaction solvent containing water;

(Composition 26) a process for the preparation of a compound of Formula (I)

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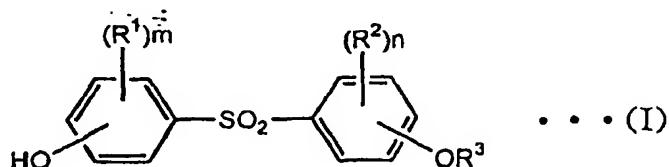


30 (wherein, R¹ and R² are each independently halogen, alkyl having 1 to 8 carbons or alkenyl having 2 to 8 carbons; m and n are each independently 0 or an integer of 1 to 4; and R³ is alkyl having 1 to 8 carbons, alkenyl having 2 to 8 carbons, cycloalkyl having 3 to 8 carbons or optionally substituted aralkyl), in which water containing 0.05 ppm or less of iron components is used as the water in the purification process for removing compounds, other than the compound of Formula (I), from the mixture containing the compound of Formula (I);

(Composition 27) a process for the preparation of a compound of Formula (I)

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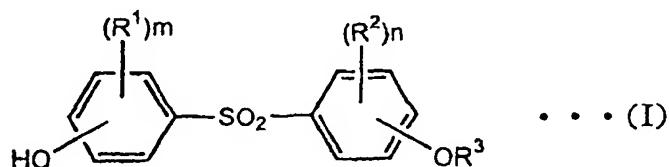


45 (wherein, R¹ and R² are each independently halogen, alkyl having 1 to 8 carbons or alkenyl having 2 to 8 carbons; m and n are each independently 0 or an integer of 1 to 4; and R³ is alkyl having 1 to 8 carbons, alkenyl having 2 to 8 carbons, cycloalkyl having 3 to 8 carbons or optionally substituted aralkyl), in which a tank with a corrosion-resistant layer over the inner wall is used in the reaction process for producing the compound of Formula (I);

(Composition 28) a process for the preparation of a compound of Formula (I)

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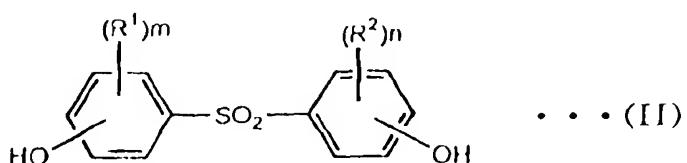
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(wherein, R¹ and R² are each independently halogen, alkyl having 1 to 8 carbons, or alkenyl having 2 to 8 carbons; m and n are each independently 0 or an integer of 1 to 4; and R³ is alkyl having 1 to 8 carbons, alkenyl having 2 to 8 carbons, cycloalkyl having 3 to 8 carbons, or optionally substituted aralkyl), in which a tank with a corrosion-resistant layer over the inner wall is used in the purification process for removing compounds, other than the compound of Formula (I), from a mixture containing the compound of Formula (I).

(Composition 29) a process for the preparation of a compound of Formula (I) according to (Composition 24) or (Composition 26) in which the corrosion-resistant layer is a layer composed of at least one material selected from the group consisting of titanium, glasses and fluorine resins.

(Composition 30) a process for the preparation of a compound of Formula (I) according to one of (Composition 24) to (Composition 29) in which the reaction process for producing the compound of Formula (I) is a process for reacting a compound represented by Formula (II)



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(wherein, R¹ and R² are each independently halogen, alkyl having 1 to 8 carbons or alkenyl having 2 to 8 carbons; m and n are each independently 0 or an integer of 1 and 4) with a compound of Formula (III)

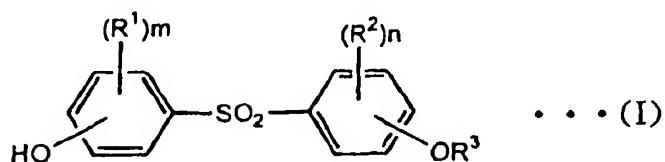
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(wherein, R³ is as defined above and X is halogen) in a solvent in the presence of a base;

(Composition 31) a process for the preparation of a compound of Formula (I)

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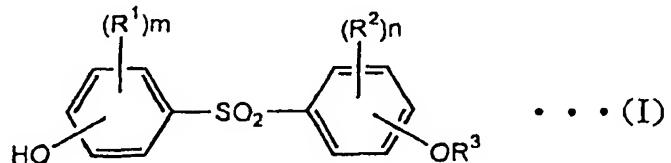
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(wherein, R¹ and R² are each independently halogen, alkyl having 1 to 8 carbons or alkenyl having 2 to 8 carbons; m and n are each independently 0 or an integer of 1 to 4; and R³ is alkyl having 1 to 8 carbons, alkenyl having 2 to 8 carbons, cycloalkyl having 3 to 8 carbons or optionally substituted aralkyl), in which a chelating agent is added in the purification process for removing compounds, other than the compound of Formula (I), from a mixture containing the compound of Formula (I);

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(Composition 32) a process for the preparation of a compound of Formula (I)

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(wherein, R¹ and R² are each independently halogen, alkyl having 1 to 8 carbons or alkenyl having 2 to 8 carbons; m and n are each independently 0 or an integer of 1 to 4; and R³ is alkyl having 1 to 8 carbons, alkenyl having 2 to 8

carbons, cycloalkyl having 3 to 8 carbons or optionally substituted aralkyl), characterized in that, in a method for producing the compound of Formula (I) with a drying process, the product is dried with mechanical stir in the drying process; (Composition 33) a process for the preparation of a compound of Formula (I) according to (Composition 32) in which the product is heated to dry under reduced pressure with mechanical stir;

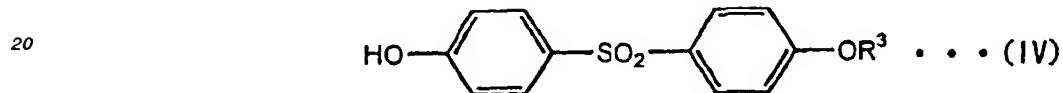
5 (Composition 34) a process for the preparation of a compound of Formula (I) according to (Composition 32) or (Composition 33) in which the compound of Formula (I) before drying is in the condition with a property of melting at a temperature below the melting point of the compound of Formula (I);

(Composition 35) a process for the preparation of a compound of Formula (I) according to one of (Composition 32) to (Composition 34) in which the compound of Formula (I) before drying is in the condition of forming a molecular compound with a solvent;

10 (Composition 36) a process for the preparation of a compound of Formula (I) according to (Composition 35) in which the solvent is an organic solvent;

(Composition 37) a process for the preparation of a compound of Formula (I) according to (Composition 36) in which the organic solvent is an aromatic hydrocarbon; and

15 (Composition 38) a process for the preparation of a compound of Formula (I) according to one of Claims 1 to 37 in which the compound of Formula (I) is a compound represented by Formula (IV)



25 (wherein, R³ is alkyl having 1 to 8 carbons, alkenyl having 2 to 8 carbons, cycloalkyl having 3 to 8 carbons or optionally substituted aralkyl).

[0022] The present invention is described in more detail in the following.

[0023] The present invention consists mainly of (Composition 1), (Composition 7), (Composition 15), (Composition 18), (Composition 24), (Composition 26), (Composition 27), (Composition 28), (Composition 31) and (Composition 32).

30 Each of them relates to a method for producing a compound of Formula (I).

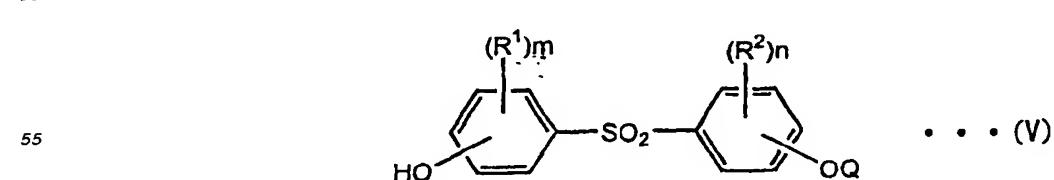
[0024] In Formula (I), R¹ and R² are each independently halogen such as fluorine, chlorine, bromine or iodine; alkyl having 1 to 8 carbons such as methyl, ethyl, n-propyl, isopropyl, n-butyl or t-butyl; or alkenyl having 2 to 8 carbons such as propenyl, isopropenyl or butenyl. m and n are each independently 0 or an integer of 1 to 4. When m and n are 1 or larger, substitution positions are not restricted.

35 [0025] In Formula (I), R³ is alkyl having 1 to 8 carbons such as methyl, ethyl, n-propyl, isopropyl, n-butyl or t-butyl; alkenyl having 2 to 8 carbons such as propenyl, isopropenyl or butenyl; cycloalkyl having 3 to 8 carbons such as cyclopropyl, cyclopentyl or cyclohexyl; or optionally substituted aralkyl such as benzyl, 4-chlorobenzyl or 2-phenylethyl. Of them, a preferred compound of Formula (I) is a compound where R is alkyl having 2 to 4 carbons such as ethyl, n-propyl, isopropyl, n-butyl or t-butyl, or optionally substituted aralkyl such as benzyl. A compound where R³ is isopropyl is particularly preferred. There are no particular restrictions on substitution positions of the hydroxyl group (OH group) and OR³ group. It is however preferable that each of them is at the para position (4 or 4' position) to the sulfonyl group. The compound can be used favorably to produce a compound of Formula (IV) where each of the groups is at the 4 or 4' position.

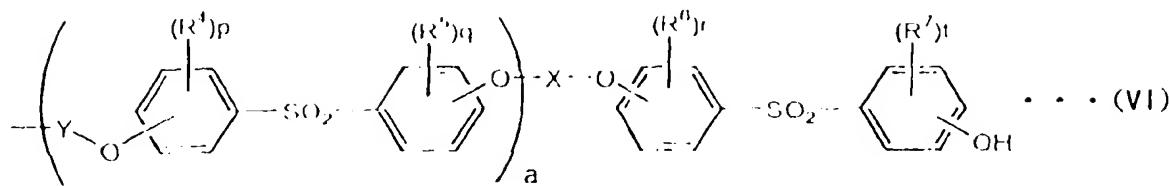
40 [0026] Actual examples of compounds represented by Formula (IV) include 4-methoxy-4'-hydroxydiphenyl sulfone, 4-ethoxy-4'-hydroxydiphenyl sulfone, 4-n-propoxy-4'-hydroxydiphenyl sulfone, 4-isopropoxy-4'-hydroxydiphenyl sulfone, 4-n-butoxy-4'-hydroxydiphenyl sulfone, 4-sec-butoxy-4-hydroxydiphenyl sulfone and 4-t-butoxy-4'-hydroxydiphenyl sulfone. Of them, 4-isopropoxy-4'-hydroxydiphenyl sulfone is particularly preferred.

45 [0027] The production methods of the present invention can be applied not only to compounds of Formula (I) but also to compounds represented by Formula (V)

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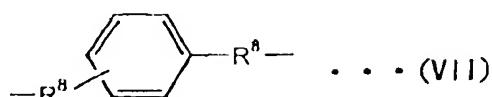


(wherein, R¹ to R⁷, m and n are as defined above, and Q is a group represented by Formula (VI)



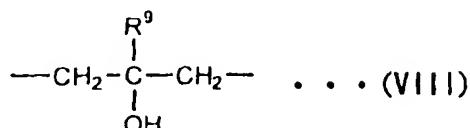
(wherein, X and Y are each independently a saturated or unsaturated, optionally substituted hydrocarbon having 1 to 12 carbons; saturated or unsaturated hydrocarbon having 1 to 12 carbons and ether bonds; a group represented by Formula (VII))

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(wherein, R⁸ is methylene or ethylene), or a group represented by Formula (VIII)

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(wherein, R⁹ is hydrogen or alkyl having 1 to 4 carbons); R⁴ to R⁷ are each independently halogen, alkyl having 1 to 8 carbons or alkenyl having 2 to 8 carbons; p, q, r and t are each independently 0 or an integer of 1 to 4, and a is 0 or an integer of 1 to 10). Particularly production methods relating to (Composition 11), (Composition 13) and (Composition 16) are preferably applied.

[0028] Actual examples of X and Y in Formula (VI) are each independently optionally substituted, saturated hydrocarbons having 1 to 12 carbons such as methylene, ethylene, trimethylene, tetramethylene, pentamethylene, hexamethylene, heptamethylene, octamethylene, nonamethylene, decamethylene, undecamethylene, dodecamethylene, methylmethylen, dimethylmethylen, methylethylene, methylene ethylene, ethylethylene, 1,2-dimethylethylene, 1-methyltrimethylene, 1-methyltetramethylene, 1,3-dimethyltrimethylene, 1-ethyl-4-methyl-tetramethylene, 2-hydroxytrimethylene, 2-hydroxy-2-methyltrimethylene, 2-hydroxy-2-ethyltrimethylene, 2-hydroxy-2-propyltrimethylene, 2-hydroxy-2-isopropyltrimethylene and 2-hydroxy-2-butyltrimethylene; optionally substituted, unsaturated hydrocarbons having 1 to 12 carbons such as vinylene, propenylene, 2-butenylene, ethynylene, 2-butynylene and 1-vinyl ethylene; and saturated or unsaturated hydrocarbons having 1 to 12 carbons and ether bonds such as ethylene oxyethylene, tetramethylene oxytetramethylene, ethylene oxyethylene oxyethylene, ethylene oxymethylene oxyethylene, and 1,3-dioxan-5,5-blsmethylene.

[0029] Actual examples of R⁸ in Formula (VII) include methylene and ethylene, and those of R⁹ in Formula (VIII) include hydrogen and alkyl having 1 to 4 carbons such as methyl, ethyl, n-propyl, isopropyl, n-butyl and t-butyl.

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[0030] Actual examples of R⁴ to R⁷ are each independently halogen such as fluorine, chlorine and bromine; alkyl having 1 to 8 carbons such as methyl, ethyl, n-propyl, isopropyl, n-butyl and t-butyl; and alkenyl having 2 to 8 carbons such as vinyl, propenyl, isopropenyl and butenyl.

[0031] The following are actual examples of compounds of Formula (V):

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1) Compounds where X and/or Y in the formula are optionally substituted, saturated hydrocarbons having 1 to 12 carbons;

4-[4-(4-hydroxyphenylsulfonyl)phenoxy-4-butyloxy]-4'-[4-(4-hydroxyphenylsulfonyl)phenoxy-3-propyloxy]diphenyl sulfone, 4,4'-bis[4-(4-hydroxyphenylsulfonyl)phenoxy-2-ethyloxy]diphenyl sulfone, 4,4'-bis[4-(4-hydroxy-

phenylsulfonyl)phenoxy-3-propyloxy]diphenyl sulfone, 4,4'-bis[4-(4-hydroxyphenylsulfonyl)phenoxy-4-butyloxy]diphenyl sulfone, 4,4'-bis[4-(4-hydroxyphenylsulfonyl)phenoxy-5-pentyloxy]diphenyl sulfone, 4,4'-bis[4-(4-hydroxyphenylsulfonyl)phenoxy-6-hexyloxy]diphenyl sulfone, 4-[4-(4-hydroxyphenylsulfonyl)phenoxy-4-butyloxy]-4'-(4-hydroxyphenylsulfonyl)phenoxy-2-ethyloxy]diphenyl sulfone, 4-[4-(4-hydroxyphenylsulfonyl)phenoxy-3-propyloxy]-4'-(4-hydroxyphenylsulfonyl)phenoxy-2-ethyloxy]diphenyl sulfone, 4,4'-bis[4-[4-(2-hydroxyphenylsulfonyl)phenoxy]butyloxy]diphenyl sulfone, 4,4'-bis[4-[2-(4-hydroxyphenylsulfonyl)phenoxy]butyloxy]diphenyl sulfone, 1,1-bis[4-(4-hydroxyphenylsulfonyl)phenoxy]methane, 1,2-bis[4-(4-hydroxyphenylsulfonyl)phenoxy]ethane, 1,3-bis[4-(4-hydroxyphenylsulfonyl)phenoxy]propane, 1,4-bis[4-(4-hydroxyphenylsulfonyl)phenoxy]butane, 1,5-bis[4-(4-hydroxyphenylsulfonyl)phenoxy]pentane and 1,6-bis[4-(4-hydroxyphenylsulfonyl)phenoxy]hexane.

2) Compounds where X and/or Y in the formula are optionally substituted, unsaturated hydrocarbons having 1 to 12 carbons;

1,2-bis[4-(4-hydroxyphenylsulfonyl)phenoxy]ethylene, 4,4'-bis[4-[4-(4-hydroxyphenylsulfonyl)phenoxy]-2-trans-butenoxy]diphenyl sulfone, 4-[4-[4-(4-hydroxyphenylsulfonyl)phenoxy]-2-trans-butenoxy]-4'-(4-hydroxyphenylsulfonyl)phenoxy-4-butyloxy]diphenyl sulfone, 4-[4-(4-hydroxyphenylsulfonyl)phenoxy]-2-trans-butyloxy]-4'-(4-hydroxyphenylsulfonyl)phenoxy-3-propyloxy]diphenyl sulfone, 4-[4-[4-(4-hydroxyphenylsulfonyl)phenoxy]-2-trans-butenoxy]-4'-(4-hydroxyphenylsulfonyl)phenoxy-2-ethyloxy]diphenyl sulfone, 1,4-bis[4-[4-(4-hydroxyphenylsulfonyl)phenoxy-2-trans-butenoxy]phenylsulfonyl]phenoxy]-cis-2-butene and 1,4-bis[4-[4-(4-hydroxyphenylsulfonyl)phenoxy-2-trans-butenoxy]phenylsulfonyl]phenoxy]-trans-2-butene.

3) Compounds where X and/or Y in the formula are saturated or unsaturated hydrocarbons having 1 to 12 carbons and ether bonds;

4,4'-bis[4-(4-hydroxyphenylsulfonyl)phenoxy]dibutyl ether, 2,2'-bis[4-(4-hydroxyphenylsulfonyl)phenoxy]diethyl ether, 4,4'-bis[4-(4-hydroxyphenylsulfonyl)phenoxy-2-ethyleneoxyethoxy]diphenyl sulfone, 2,2'-bis[4-[4-[4-(4-hydroxyphenylsulfonyl)phenoxy-2-ethyleneoxyethoxy]phenylsulfonyl]phenoxy]diethyl ether, 2,4'-bis[2-(4-hydroxyphenylsulfonyl)phenoxy-2-ethyleneoxyethoxy]diphenyl sulfone, 2,4'-bis[4-(2-hydroxyphenylsulfonyl)phenoxy-2-ethyleneoxyethoxy]diphenyl sulfone, 4,4'-bis[3,5-dimethyl-4-(3,5-dimethyl-4-hydroxyphenylsulfonyl)phenoxy-2-ethyleneoxyethoxy]diphenyl sulfone, and 4,4'-bis[3-allyl-4-(3-allyl-4-hydroxyphenylsulfonyl)phenoxy-2-ethyleneoxyethoxy]diphenyl sulfone.

4) Compounds where X and/or Y in the formula are groups represented by Formula (VII);

α,α' -bis[4-(4-hydroxyphenylsulfonyl)phenoxy]-p-xylene, α,α' -bis[4-(4-hydroxyphenylsulfonyl)phenoxy]-m-xylene, α,α' -bis[4-(4-hydroxyphenylsulfonyl)phenoxy]-o-xylene, α,α' -bis[4-[4-[4-(4-hydroxyphenylsulfonyl)phenyl-1,4-phenylenebismethyleneoxy]phenylsulfonyl]phenoxy]-p-xylene, α,α' -bis[4-[4-[4-(4-hydroxyphenylsulfonyl)phenyl-1,3-phenylenebismethyleneoxy]phenylsulfonyl]phenoxy]-m-xylene, α,α' -bis[4-[4-(4-hydroxyphenylsulfonyl)phenyl-1,2-phenylenebismethyleneoxy]phenylsulfonyl]phenoxy]-o-xylene, 4,4'-bis[4-(4-hydroxyphenylsulfonyl)phenyl-1,4-phenylenebismethyleneoxy]diphenyl sulfone, 4,4'-bis[4-(4-hydroxyphenylsulfonyl)phenyl-1,3-phenylenebismethyleneoxy]diphenyl sulfone, 4,4'-bis[4-(4-hydroxyphenylsulfonyl)phenyl-1,2-phenylenebismethyleneoxy]diphenyl sulfone, 4,4'-bis[3,5-dimethyl-4-(3,5-dimethyl-4-hydroxyphenylsulfonyl)phenyl-1,4-phenylenebismethyleneoxy]diphenyl sulfone, 4,4'-bis[3,5-dimethyl-4-(3,5-dimethyl-4-hydroxyphenylsulfonyl)phenyl-1,3-phenylenebismethyleneoxy]diphenyl sulfone, 4,4'-bis[3,5-dimethyl-4-(3,5-dimethyl-4-hydroxyphenylsulfonyl)phenyl-1,2-phenylenebismethyleneoxy]diphenyl sulfone, 4,4'-bis[3-allyl-4-(3-allyl-4-hydroxyphenylsulfonyl)-1,4-phenylenebismethyleneoxy]diphenyl sulfone, 4,4'-bis[3-allyl-4-(3-allyl-4-hydroxyphenylsulfonyl)-1,3-phenylenebismethyleneoxy]diphenyl sulfone and 4,4'-bis[3-allyl-4-(3-allyl-4-hydroxyphenylsulfonyl)-1,2-phenylenebismethyleneoxy]diphenyl sulfone.

5) Compounds where X and/or Y in the formula are groups represented by Formula (VIII);

4,4'-bis[4-(4-hydroxyphenylsulfonyl)phenoxy-2-hydroxypropyloxy]diphenyl sulfone and 1,3-bis[4-[4-[4-(4-hydroxyphenylsulfonyl)phenoxy-2-hydroxypropyloxy]phenylsulfonyl]phenoxy]-2-hydroxypropane.

[0032] Of these compounds, preferred are where a is 0 or an integer of 1 to 3, and X and/or Y are -CH₂CH₂-O-CH₂CH₂- or -CHCH=CHCH₂-

[0033] A compound of Formula (V) can be produced using, instead of a compound of Formula (III), a compound represented by Formula (IX)



(wherein, A1 to A4 are each independently halogen), according to a method for producing a compound of (I) which is described later. The product is a single compound or a mixture of several compounds. The present invention is applicable to separate or purify these compounds from starting materials and byproducts.

[0034] There are no particular restrictions on methods for synthesizing compounds represented by Formula (I) (hereinafter referred to as Compound (I)), except inventions relating to (Composition 15) and (Composition 18). A method for reacting a compound represented by Formula (II) (hereinafter referred to as Compound (II)) with a compound represented by Formula (III) (hereinafter referred to as Compound (III)) in a solvent in the presence of an alkali is exemplified as most preferred.

[0035] In Formula (III), X is halogen such as chlorine, bromine or iodine. Actual examples of compounds of Formula (III) include alkyl halides such as methyl iodide, ethyl iodide, ethyl bromide, n propyl iodide, n propyl bromide, n propyl chloride, isopropyl iodide, isopropyl bromide, isopropyl chloride, n butyl iodide, n butyl bromide, sec butyl iodide, sec butyl bromide, t butyl iodide, t butyl bromide, n pentyl iodide, n pentyl bromide, n hexyl iodide and n hexyl bromide, alkenyl halides such as allyl chloride, allyl bromide, allyl iodide, crotyl chloride and crotyl bromide, cycloalkyl halides such as cyclopropyl iodide, cyclopropyl bromide, cyclopropyl chloride, cyclopentyl iodide, cyclopentyl bromide, cyclopentyl chloride, cyclohexyl iodide, cyclohexyl bromide and cyclohexyl chloride, and aralkyl halides such as benzyl iodide, benzyl bromide, benzyl chloride, 4 chlorobenzyl iodide, 4 methylbenzyl bromide, 3 chlorobenzyl chloride, (1-phenyl)ethyl iodide, (1 phenyl)ethyl bromide, 2 phenylethyl bromide, 2 phenylethyl chloride and 3 phenylpropyl bromide.

[0036] Of them, a preferred compound of Formula (III) is where X is bromine. It is particularly favorable to use iso propyl bromide. An amount of Compound (III) used is usually in the range of 1 to 3 moles, preferably 1 to 1.5 moles, to a mole of Compound (II).

[0037] Actual examples of bases used for the reaction include alkali metal hydroxides such as sodium hydroxide and potassium hydroxide, alkaline earth metal hydroxides such as magnesium hydroxide and calcium hydroxide, alkali metal carbonates such as calcium carbonate; and organic amines such as triethylamine, pyridine and diazabicyclo [5.4.0]undec-7-ene. Of them, alkalis including alkali metal hydroxides such as sodium hydroxide are particularly preferred. An amount of a base used is usually in the range of 1 to 5 moles, preferably 1.5 to 3 moles, to a mole of Compound (II).

[0038] Examples of solvents used include water, amides such as N,N dimethylformamide and N,N dimethylacetamide; alcohols such as methanol, ethanol and propanol; and two-phase mixture solvents such as water-toluene, water-xylene and water-benzene. An amount of a solvent used is usually in the range of 0.1 to 10 parts by weight to a part by weight of Compound (II).

[0039] A reaction method is, for example, by adding Compound (III) to a solution of an alkali salt of Compound (II). There are no particular restrictions on how to add Compound (III). Examples are a method of dropping a fixed amount of Compound (II) continuously into a reaction solution and adding Compound (III) little by little over several times. A reaction is carried out usually at a temperature between room temperature and the boiling point of the solvent, preferably between 45 to 80°C, and normally finishes in about 1 to 25 hours.

[0040] A method for producing a compound of Formula (I) in the present invention is a general term for all processes from starting materials to the completion of a product, covering a reaction process for reacting starting materials to give a reaction mixture containing Compound (I), such as a process for reacting Compound (II) with Compound (III), as well as a purification process, such as separation of the materials and impurities; processes for separating Compound (I) after the completion of the purification process, such as crystallization, distillation, filtration and recrystallization; and processes particularly required for industrial production, such as drying and solvent recovery. Actual examples are a combination of a series of processes of pretreatment, reaction, purification, crystallization, filtration, drying and solvent recovery, and a combination of each process twice or more.

[0041] The reaction mixture thus obtained contains Compound (I) as well as impurities such as unreacted Compound (II), unreacted Compound (III) and a byproduct of 4,4'-dihydroxydiphenyl sulfone diether. It is therefore necessary to separate these impurities from the reaction mixture, that is, purification of the reaction mixture, in order to produce the target compound of high purity.

[0042] The production method of the present invention is described in detail, using as an example, when a reaction mixture of 4,4'-dihydroxydiphenyl sulfone (hereinafter referred to as BPS) and Compound (III) is purified to isolate the target compound, that is, a compound represented by Formula (V) (hereinafter referred to as Compound (V)).

[0043] To react BPS with Compound (III) in the presence of a base, it is usually carried out in a way that, for example, a BPS salt produced from BPS and a base is reacted with Compound (III). Solubility of the BPS salt in non-polar organic solvents is low so that the reaction is usually carried out in a polar solvent, water or a mixed solvent of water and

organic solvents. BPS has two positions to form a salt with a base in one molecule. A problem is therefore how to control the production of a byproduct of 4,4'-dihydroxydiphenyl sulfone diether (hereinafter sometimes referred to as the diether) in the reaction.

[0044] For example, thanks to the fact that a salt of Compound (V) with a base (alkali) (hereinafter referred to as Compound (V) salt) is less soluble in water than the said di-salt compound is, there is a method that Compound (III) is reacted with the di-salt compound in a saturated or nearly saturated aqueous solution to deposit the Compound (V) salt to remove to the outside of the reaction system as crystals.

[0045] Another example is that a reaction is carried out in a two-phase system of water and a water-nonmiscible organic solvent, which dissolves Compound (V) to some extent, pH is controlled to restrain the formation of the said di-salt and Compound (V) salt, and produced Compound (V) is dissolved in the organic solvent to remove into the outside of the system.

[0046] In either method, after the reaction is completed, the reaction mixture contains impurities of BPS, the diether and others. If such impurities are contained, it is difficult to isolate the target compound of high purity as crystals only by operations such as recrystallization, because the structures of the impurities are similar to that of the target compound. A method is applied for separating the impurities by pH adjustments, as BPS, Compound (V) and the diether are different in acidity.

[0047] An operation of purifying the said reaction mixture to isolate the target compound is carried out, for example, according to steps described below:

20 (a) First, remove unreacted Compound (III).

The reaction solution usually contains unreacted Compound (III). Compound (III) is generally unstable in water, particularly in an aqueous alkaline solution, and is more unstable and easily decomposes when heated. As described above, when water is used as a reaction solvent and an alkali as a base, Compound (III) has to be used in an excessive amount because of its easy decomposition during the reaction. Compound (III) decomposes to generate an acid if it is present in post-treatment processes, such as purification, after the reaction is completed. The acid reacts with the alkali to reduce pH of the reaction solution.

The pH reduction is local and its change is small. An accurate pH adjustment is however particularly required, as described later, in order to separate the target compound into the organic layer and impurities into the aqueous alkali layer precisely. Non-uniform pH values or pH values different from preset values result in difficulties in complete separation of the target compound from starting materials and byproducts.

In this reaction, the reaction solution was sometimes colored in the process for purifying the reaction solution after the reaction was completed and the product, Compound (V), also colored. Once the product is colored, a problem is difficulties in decoloring.

The inventors have studied causes of the coloring in detail. As a result, it was considered that a reason why the reaction solution was colored in the purification process was because heavy metal ions, such as iron ions, contained in industrial water used as a reaction solvent and as water in the purification process or dissolved from an SUS reaction tank, formed chelate compounds with compounds having phenolic hydroxyl groups, such as Compound (V), and the chelate compounds were the cause of the coloring. It was also considered that the chelate compounds, which caused coloring, were easily formed because the pH value of the reaction solution lowered locally to produce a pH region where a compound having a phenolic group could form a chelate compound with a heavy metal ion. It is therefore necessary to control pH precisely and uniformly in the purification process in order to efficiently prevent the formation of the chelate compounds and to produce non-colored products.

The present invention has made it possible to prevent the pH value of the reaction solution from changing due to the decomposition of Compound (III) so as to adjust the pH accurately, by providing a process for removing unreacted Compound (III) contained in the reaction solution in the process for purifying the reaction solution after the reaction is completed.

Compound (III) may be removed after the completion of the reaction and before the isolation of the target compound. In the present invention, it is favorable to remove Compound (III) after the completion of the reaction and before the said pH adjustment of the aqueous layer, from the viewpoint of accurate pH adjustment with control of pH changes to the minimum. It is more favorable to remove unreacted Compound (III) after the reaction is completed and before the diether is extracted with organic solvents for removal. In other words, it is preferable to provide the process for removing Compound (III) immediately after the reaction process.

There are no particular restrictions on methods for removing Compound (III). Examples include (1) after the reaction is completed, the reaction solution is heated to evaporate Compound (III) to remove; and (2) after the reaction is completed, an extract solvent, such as benzene or toluene, is added to the reaction solution to extract Compound (III) to remove.

Of them, Method (1) is simpler in the present invention. In the operation of evaporating for removal in Method (1), it is preferable to distill out Compound (III) together with the solvents used for the reaction. Particularly when

Water is used as a reaction solvent if it is favorable to add a solvent azeotropic with water, such as, toluene or benzene, and to distill out Compound (III) together with the mixed solvent because Compound (III) can be recovered at a lower temperature with the minimum decomposition. Method (1) can be carried out at the atmospheric pressure or under reduced pressure. If performed under reduced pressure, unreacted Compound (III) can be evaporated to remove at a lower temperature so that pH changes due to the decomposition of Compound (III) can be controlled.

Compound (III) removed from the reaction solution may be recovered or obtained by other means, for reuse.

In the production method of Compound (I) with a process for removing Compound (III) after Compound (II), such as, BPS, and Compound (III) are reacted in 0.3 to 1.5 parts by weight of an aqueous solvent to a part by weight of Compound (II) in the presence of 1.5 to 3 moles of an alkali to a mole of Compound (II) followed by distillation of Compound (III), if Compound (III) is heated to distill out and then water is further added to distill Compound (III) to remove, the compound is efficiently recovered and production of impurities, such as, the diether, can be controlled.

It is favorable to add water separately over several times. In addition, an amount of water added at the beginning is in the range of 0.03 and 0.1 parts by weight, more preferably 0.04 and 0.08 parts by weight, to a part by weight of Compound (II). A favorable way is to control an amount of water added at the beginning for a sufficient recovery of Compound (III). If less than 0.03 parts by weight, Compound (III) cannot be distilled out sufficiently. If exceeds 0.1 parts by weight, impurities, such as the diether, are more produced. An amount of water added at the second time and after may be the same as that at the beginning, or larger if Compound (III) remains in small amount.

The smaller an amount of Compound (III) remains in the reaction solution after Compound (III) is distilled out, the more preferable. It becomes more difficult to completely remove the compound by distillation with a larger reaction scale. Compound (III) remaining in the reaction solution after distillation may be contained, for example, in an organic solvent used in the process for crystallizing Compound (I) (Compound (V)) from the organic solvent, via post processes. The organic solvent used for the crystallization is often recovered for reuse after Compound (I) is filtrated. Reuse of the solvent containing a large amount of Compound (III), as described above, causes problems such as coloring of Compound (I) because of decomposition of Compound (III) in various processes. It is therefore necessary to reduce the amount of Compound (III) in the organic solvent. It is usually preferable to control to 1% by weight or less. It is favorable to distill out Compound (III) so that the content of Compound (III) in the organic solvent used in the crystallization process is 1% by weight or less.

(b) Next, a water nonmiscible solvent and, if required, water and/or an alkali (aqueous) are added to the reaction mixture to make a two-phase solution of organic and aqueous layers. When a polar solvent is used for the reaction, it is preferable to carry out this operation after the polar solvent is recovered or removed. It is also favorable to adjust pH to 8 or above to completely separate the diether from the Compound (V) salt. There are no particular restrictions on the said water-nonmiscible solvents if they are organic solvents that do not mix with water. Aromatic hydrocarbons such as toluene, xylene and benzene are preferably used. The separation operation separates the diether having no phenolic hydroxyl group into the organic layer and the target compound into the aqueous layer.

The separation operation is favorably carried out at a temperature above the crystallization temperature, usually in the temperature range of 70 and 90°C, from the viewpoint of preventing the target compound, impurities and the like from crystallizing. An amount of the water-nonmiscible organic solvent used is usually in the range of 0.5 and 5 ml to 1g of BPS used as a starting material. Compound (V) produced and unreacted BPS are both soluble, but the diether is insoluble, in aqueous alkaline solutions. Without using a water-nonmiscible organic solvent, the diether can be removed in a way that a reaction mixture obtained after organic solvents and the like are removed (or after the reaction is completed if water is used as a reaction solvent) is adjusted pH to 8 or above and deposited diether is filtered off.

(c) Then, the aqueous layer containing the target compound is separated. A water-nonmiscible organic solvent and, if required, water are added to the obtained aqueous layer to make a two-phase solution of organic and aqueous layers. The aqueous layer is adjusted pH to a preset value (P1). The adjustment of pH to the preset value (P1) separates the target compound into the organic layer and impurities including BPS into the aqueous alkali layer. The pH value is usually adjusted by adding an acid or alkali to the aqueous layer. In this case, after the pH of the aqueous layer is adjusted, a water-nonmiscible organic solvent may be added to extract the target compound.

Examples of acids for use include hydrochloric acid, sulfuric acid and nitric acid. Sodium hydroxide and potassium hydroxide are exemplified as alkalis for use. An alkali, when used, can be added in a form of aqueous solution. It is preferable to add an acid or alkali little by little in amount while sufficiently stirring the whole mixture from the viewpoint of prevention of drastic pH changes and precise pH adjustment. The preset value (P1) of pH is usually in the range of 8 and 9, preferably 8.3 and 8.7. In this case, to prevent the target compound and impurities

from crystallizing, it is favorable to add a water-nonmiscible organic solvent and water, as required, to the reaction solution and to carry out the separation operation while keeping a temperature above the crystallization temperature, usually in the range of 70 and 90°C.

5 (d) Furthermore, water and, if required, a water-nonmiscible organic solvent are added to the organic layer obtained after the said aqueous layer is removed, to make again a two-phase solution, and the aqueous layer is adjusted pH to a preset value (P2). Particularly when the reaction mixture is high in concentration, a third layer in which the target compound is not completely separated from BPS and others may be formed near the interface between the organic and aqueous layers. In this case, it is necessary to remove the completely separated aqueous layer, and the remaining organic and third layers are adjusted pH for completely separating BPS from the target compound.

10 In the prior art, water and a water-nonmiscible organic solvent are added to a reaction product containing the target compound to make a two-phase solution, pH of the aqueous layer is adjusted to a preset value to separate the organic layer, and the target compound is obtained from the organic layer. However, particularly when a reaction mixture of high concentration is purified, for example, when a reaction mixture obtained from a reaction of materials of high concentrations or a reaction mixture containing a high concentration of inorganic salt is purified without diluting it much, it has been difficult to separate the target compound from impurities with only one pH adjustment.

15 The inventors have studied causes of the above difficulty. As a result, the following were considered to be causes of the difficulty in the complete separation of the target compound from impurities:

20 (1) A difference in acidity between the phenolic hydroxyl groups of Compound (V) and BPS is small. Therefore, it is impossible to separate the target compound from BPS and others completely without an accurate pH adjustment.

25 (2) Solubilities of both of the target compound and BPS in water and water-nonmiscible solvents are relatively small. Because of this, when a water-nonmiscible solvent is added to a mixture of these to make a two-phase solution, particularly when a solution of the mixture of high concentration is used, a third, intermediate layer in which Compound (V) and BPS are mixed without being separated is formed near the interface between the aqueous and organic layers. Therefore, their separation is insufficient. A ratio of the layer in the whole solution tends to become larger as a reaction product is higher in concentration.

30 (3) Due to the effect of salting out by a large amount of inorganic salts produced from the reaction of Compound (III) with BPS, BPS salts do not dissolve in the aqueous layer completely and cannot dissolve in the organic layer either so as to take Compound (V) in to form the third layer.

(4) On the other hand, when the target compound is produced at an industrial scale, fairly large amounts of water and a water-nonmiscible organic solvent cannot be added to the reaction solution because of work efficiency and capacities of reaction and treatment tanks.

35 (5) Therefore, it may be often the case that it is difficult to completely separate the target compound, Compound (V), from BPS when a series of operations of adjusting pH of the aqueous layer to be treated to a preset value and separating the organic layer is carried out only once.

40 Based on the above facts, in the present invention, a series of operations consisting of a pH adjustment of the aqueous layer of the two-phase solution and separation of the organic layer is repeated several times in order to produce the target compound of high purity in high yield.

The present invention provides methods for producing 4,4'-dihydroxydiphenyl sulfone monoethers, in which the target compound of high purity is isolated efficiently from a mixture even if the mixture contains the target compound and impurities of high concentrations.

45 When the reaction product obtained from a reaction of BPS with a compound of Formula (III) in a solvent in the presence of a base is purified, only a requirement is an addition of the operations of the pH adjustment of the aqueous layer of the two-phase solution and separation of the organic layer, without changing the current production lines at all.

50 Therefore, according to the purification method of the present invention, 4,4'-dihydroxydiphenyl sulfone monoethers of extremely high purity can be produced advantageously in industrial production.

The second pH adjustment can be done by an operation similar to that of the first. An adjustment of pH of the aqueous layer to a preset value (P2) removes impurities contained in the organic layer into the aqueous layer. The pH value (P2) can be set to the same value as that of P1. It is however preferable to set P2 very slightly different from the pH value of the first adjustment in order to completely separate the target compound from BPS. Setting P2 to a value lower than P1 is preferred. For example, P1 is set in the range of 8.4 and 8.7 and P2 in the range of 8.3 and 8.6. A series of the operations of the pH adjustment of the aqueous layer of the two-phase solution and separation of the organic layer can be repeated further, if required.

55 As described above, if a series of the operations of adjusting pH of the aqueous layer to the preset values (P1

and I⁽²⁾), and separating the organic layer is repeated twice or more in the process, for purifying the reaction solution. 4,4'-dihydroxydiphenyl sulfone monoether, of extremely high purity can be isolated from the reaction mixture.

In the process of purification with water and an organic solvent for removing impurities, other than Compound (I), from the reaction solution as described above, by adjusting pH of the reaction solution produced from the reaction of Compound (II) with Compound (III) in a solvent in the presence of a base, it is preferable to set a concentration of the compound of Formula (III) in the organic solvent to 5% by weight or less, more preferably 2% by weight or below, and furthermore preferably 1% by weight or less. An organic solvent used for a purification process, such as that mentioned above, is often an organic solvent, for example, that is used in a crystallization process, and recovered for reuse. In the case, the solvent may contain compounds involved in the reaction. Of them, Compound (III) easily decomposes when contacts with water, alkali or the like. Use of an organic solvent containing such a compound for a purification process may cause problems, including coloring of Compound (I). It is necessary to reduce the content of such an impurity as much as possible. To reduce an amount of Compound (III) contained in an organic solvent to be used in the purification process, a new organic solvent can be used instead of a recovered organic solvent for reuse. A recovered solvent after precision distillation may be also used. For an efficient production overall, however, it is preferable to distill out unreacted Compound (III) to the outside of the system as much as possible so as not to remain any, in the process, for distilling Compound (III) to remove.

(e) Finally, the organic layer is separated from the two phase solution after the final pH adjustment is carried out, washed with water if necessary, and cooled to deposit crystals. The crystals are separated by filtration, washed with water and dried to give the target compound.

[0048] Compound (I) may often form a molecular compound particularly with a crystallization solvent in the crystallization process for taking out the compound as crystals, because of its structural and electronic properties. If Compound (I) forming a molecular compound with the crystallization solvent or the like is filtrated and then heated to dry under reduced pressure while leaving to stand, the compound may melt simultaneously when the crystalline form as the molecular compound collapses, and form amorphous block particles with surrounding crystals in the condition of keeping the solvent inside, halfway through the process that the solvent breaks the bond with Compound (I) and vaporizes. There is no problem if the compound melts at a temperature above the melting point of Compound (I), because Compound (I) itself does not crystallize even if releasing the solvent molecule. In case of melting below the melting point of Compound (I), Compound (I) crystallizes after the molecular compound melts and the solvent vaporizes. Because of this, it is often the case that part of the solvent does not vaporize completely and is taken in the inside of block particles. It is very difficult to pulverize such block particles unless considerable force is applied from the outside. The solvent taken in the inside cannot be removed completely.

[0049] Therefore, the present invention is characterized in drying with mechanical stir. It is particularly favorable to dry by heating under reduced pressure with mechanical stir.

[0050] Actual examples of solvents to form molecular compounds with Compound (I) include water; alcohols such as methanol, ethanol, n-propanol, isopropanol and 1,2-butanediol; ketones such as acetone, methyl ethyl ketone and acetyl acetone; nitriles such as acetonitrile and benzonitrile; ethers such as diethyl ether, dibutyl ether, tetrahydrofuran and dioxane; esters such as methyl acetate, ethyl acetate and butyl acetate; amides such as N,N-dimethylformamide and N,N-dimethylacetamide; halogenated hydrocarbons such as dichloromethane, chloroform, 1,2-dichloroethane and chlorobenzene; aromatic hydrocarbons such as dimethyl sulfoxide, benzene, toluene and xylene; and aliphatic hydrocarbons such as hexane, cyclohexane and decalin. Particularly, a molecular compound formed with an aromatic hydrocarbon, such as benzene or toluene, is preferably dried according to the method of the present invention, because the compound is apt to melt during this process.

[0051] There are no particular restrictions on a ratio of Compound (I) and a solvent that form a molecular compound. Concretely, the ratio is in the range of 0.1 to 10 moles of a solvent to a mole of Compound (I).

[0052] In the present invention, "mechanical stir" refers to stirring a molecular compound with a stirring apparatus. Actual examples of stirring apparatus include those with stirring blades such as inclined paddle blades, flat paddle blades, propeller blades, anchor blades, faudler blades, turbine blades, bull margin blades, max blend blades, full zone blades, ribbon blades, super mix blades or inter mix blades; and those with rotary disks such as disk, notched disk or screw.

[0053] A vacuum stirring apparatus with a stirring apparatus may be of batch or continuous type. Actual examples include Paddle Dryer (made by Nippon Kansaki Co., Ltd), Multifin Processor (made by Nara Kikai Seisakusho Co., Ltd), Plough Share Mixer (made by Taiheiyo Kiko Co., Ltd) and Inklandent Dryer (made by Tukishima Kikai Co., Ltd).

[0054] A stirring speed depends on a type of stirring apparatus used and other conditions. Approximately 1 to 10 revolutions/minute is usually satisfactory.

[0055] A heating temperature differs, depending on a type of solvent to vaporize. For example, when toluene is used, it is preferably in the range of room temperature and 100°C, and particularly favorably from 50 to 90°C.

[0056] Drying under reduced pressure is usually carried out at 200 mmHg or below, and preferably 150 mmHg or less in particular.

[0057] The content of the solvent before and after drying can be measured by such a means as calorimetric analysis and differential thermal analysis.

5 [0058] The present invention is characterized in use of a solvent, particularly water, containing 0.05 ppm or less of iron components in the process for producing Compound (I). It is preferable to use a solvent, such as water, containing a very small amount of iron components throughout the production processes. However, it is not always necessary to use it in all processes. As described above, an iron component can form a complex with Compound (I) particularly when pH is between 5 and 7. It is therefore favorable to use water containing a very small amount of iron components 10 particularly in the process where pH control is difficult. Thus, use of a solvent, such as water, containing a very small amount of iron components is preferred in the reaction process for producing Compound (I) and/or in the purification process for removing compounds, other than Compound (I), from the reaction mixture containing Compound (I). In the present invention, "an amount of iron components contained" refers to a content of iron, iron compounds and iron ions 15 (including ions with iron atoms) in water used and the like. These iron components, in the form existing in water and the like or reacting with acids or alkalis to become iron ions or ions containing iron atoms, can form colored complexes with Compound (I).

20 [0059] Examples of methods for obtaining a solvent containing 0.05 ppm or less of iron components include known methods in the art, such as, in the case of water, distillation of industrial water (distilled water), and purification of industrial water through columns filled with substances having a function to catch iron components, such as ion exchange resins (water passed through a water purifier, ion exchanged water and the like). An amount of iron components contained in water can be measured with such measuring equipment as UV or visible light spectrophotometer, inductively coupled high-frequency plasma-atomic emission spectroscope, atomic absorption analyzer, photoelectric photometer and colorimeter.

25 [0060] The present invention is characterized in production of Compound (I) using reaction or purification tanks with corrosion-resistant layers on the inner walls (which may hereinafter refer to as "Tanks"). It is preferable to use tanks with corrosion-resistant layers throughout the production processes. However, it is not always necessary to use them in all processes. It is efficient to use Tanks when there is a risk of elution of iron components and the like, which cause coloring of Compound (I), from a tank into the solution due to corrosion. It is therefore preferable to use reaction tanks 30 with corrosion-resistant layers in the reaction process for producing Compound (I) and/or in the purification process for removing compounds, other than Compound (I), from the reaction mixture containing Compound (I).

[0061] There are no particular restrictions on materials used for the corrosion-resistant layers, if they are not corroded with acids, such as sulfuric acid, or alkalis, such as sodium hydroxide, used in the reaction or purification process.

35 [0062] Examples of corrosion-resistant materials include corrosion-resistant metals such as titanium, zirconium, tantalum, niobium and nickel; glasses such as borosilicate glass, neutral glass, quartz glass and alkali-resistant glass; inorganic materials such as enamel; organic materials including fluorine resins such as ethylene tetrafluoride resins (PTFE or TFE), ethylene tetrafluoride-perfluoroalkoxy vinyl ether copolymers (PFA), ethylene tetrafluoride-propylene hexafluoride copolymers (FEP), polychlorotrifluoroethylene (PCTFE), ethylene tetrafluoride-ethylene copolymers (ET-FE), chlorotrifluoroethylene-ethylene copolymers (ECTFE), polyvinylidene fluoride (PVDF) and polyvinyl fluoride (PVF).

40 [0063] An example of a method for forming a corrosion-resistant layer on the inner wall is lining or coating of a corrosion-resistant material on the inner wall. As for methods for lining or coating, when a glass is used, an example is glass lining that a vitreous glaze is baked on the surface of the base material (steel plate) composing the tank. When a fluorine resin is used, coating by baking a powder and sheet lining using a glass cloth are exemplified. Of them, a tank whose inner wall is lined or coated with a glass or fluorine resin is preferably used from the viewpoint of heat resistance, durability and others. It is more favorable to use a tank with the inner wall lined with a glass (commonly known as GL).

45 [0064] In the present invention, any of the following methods are applicable: (a) a reaction is carried out in an SUS tank as before, using water with a content of iron components of 0.05 ppm or less as a reaction solvent and/or purification solvent; (b) a reaction is carried out in a tank with a corrosion-resistant layer on the inner wall, using industrial water as before; or (c) water containing 0.05 ppm or less of iron components is used as a reaction solvent and/or a purification solvent and a tank with a corrosion-resistant layer on the inner wall also used. The method (c) is particularly preferred from the viewpoint of production of non-colored; highly pure diphenyl sulfone compounds more securely.

50 [0065] The reaction mixture may be colored in the purification process for removing compounds, other than Compound (I), from the reaction mixture containing Compound (I). This is considered to occur because metal ions including iron ions, nickel ions and chromium ions, that dissolve out from an SUS reaction vessel, which is usually used as a reaction vessel, in the process for reacting Compound (II), such as BPS, with Compound (III), or that are contained in a very small amount in water (industrial water) used in the process for purifying the reaction mixture, combine with phenolic compounds, such as Compound (I), to form complexes, which color the reaction solution. It is difficult to

decolor the solution once colored, even if purified repeatedly afterward. Because of this, in the present invention, a chelating agent is added to the reaction mixture in the process for purifying the reaction mixture, and captures the metal ions by chelation for preventing the coloring.

[0066] There are no particular restrictions on chelating agents used, if they are compounds to bind with metal ions, to form chelates. Actual examples include compounds obtained from reactions of compounds having amino groups, such as ammonia, polyamine and amino acids, with carbon disulfide, halogenated carboxylic acids, halogenated alcohols, and the like, and salts of these compounds, and dithiocarbamates, dimethylglyoxime, dithizone, bipyridine and phenanthroline.

[0067] Examples of the said polyamines include ethylenediamine, N-methylethylenediamine, N,N'-dimethylethylenediamine, 1,2-diaminopropane, 1,3-diaminopropane, diethylenetriamine, triethylenetetramine, tetramethyl enepentamine and pentamethylenehexamine.

[0068] Examples of halogenated carboxylic acids include monochloroacetic acid, monobromoacetic acid, monoiodoacetic acid, 1-chloropropionic acid, 2-chloropropionic acid, 1-bromopropionic acid and 2-bromopropionic acid.

[0069] Examples of halogenated alcohols include 1-chloroethanol, 2-chloroethanol, 1-bromoethanol, 2-bromoethanol, 1-chloropropanol, 2-chloropropanol, 2-chloroisopropanol, 3-chloropropanol, 1-bromopropanol, 2-bromopropanol, 2-bromoisopropanol and 3-bromopropanol.

[0070] Actual examples of chelating agents include dithiocarbamates such as sodium dithiocarbamate and potassium dithiocarbamate; acetic acid derivatives of amines such as ethylenediaminetetraacetic acid (EDTA), hydroxyethylimidodiacetic acid (HEIDA), nitrilotriacetic acid (NTA), hydroxyethylmethylenediaminetriacetic acid (HEDTA), diethylenetriaminepentaacetic acid (DTPA) and triethylenetetraminehexaacetic acid (TTHA), and salts of these acetic acid derivatives (for example, alkali metal salts such as sodium and potassium, alkaline earth metal salts such as calcium and magnesium; and ammonium salts); ethanolamines such as ethanolamino, N,N'-bis(2-hydroxyethyl)ethylenodiamino, N,N',N'''-tris(2-hydroxyethyl)ethylenediamine and dihydroxyethylglycine (DEEG), salts of dithiocarbamic acid derivatives of polyamines such as N,N'-bis(dithiocarboxy)ethylenediamine sodium salt, N,N'-bis(dithiocarboxy)ethylenodiamine potassium salt, N,N'-bis(dithiocarboxy)trimethylenediamine sodium salt, N,N'-bis(dithiocarboxy)trimethylenodiamine potassium salt, N,N'-bis(dithiocarboxy)diethylenetriamine sodium salt, N,N'-bis(dithiocarboxy)diethylenetriamine potassium salt, N,N',N'''-tris(dithiocarboxy)diethylenetriaminosodium salt, N,N',N'''-tris(dithiocarboxy)diethylenetriamine potassium salt, N,N'-bis(dithiocarboxy)triethylenetetramine sodium salt, N,N'-bis(dithiocarboxy)triethylenetetramine potassium salt; dimethylglyoxime, dithizone, bipyridine and phenanthroline.

[0071] Of these chelating agents, preferred are chelating agents forming water-soluble chelates (water soluble chelating agents) represented by chelating agents obtained by reacting ammonia or polyamine with halogenated carboxylic acids and/or halogenated alcohols; and salts of these agents. Use of EDTA or its salts is particularly preferred because of easy acquisition, handling, easy separation and the like.

[0072] Examples of EDTA salts include EDTA disodium salt, EDTA trisodium salt, EDTA tetrasodium salt, EDTA dipotassium salt, EDTA tripotassium salt, EDTA tetrapotassium salt, EDTA calcium salt, EDTA tricalcium salt, EDTA diammonium salt and EDTA magnesium dipotassium salt. When a water-soluble chelating agent is added to the reaction mixture, the chelates produced are water-soluble and are not taken in the crystals of 4,4'-dihydroxydiphenyl sulfone. Thus, the target compound that is completely decolorized is produced.

[0073] A chelating agent can be added at any one of the following stages: (a) after the completion of the reaction and before the removal of unreacted Compound (III), (b) after the removal of Compound (III) and before the removal of 4,4'-dihydroxydiphenyl sulfone diethers, (c) after the removal of 4,4'-dihydroxydiphenyl sulfone diethers and before the removal of unreacted Compound (II) with pH adjustments, and (d) after the removal of unreacted Compound (II) with pH adjustments. Of them, (d) is preferred, that is, a chelating agent is added after pH is adjusted to remove unreacted Compound (II). An addition of a water-soluble chelating agent at the same time when water is added to the reaction mixture is particularly preferred because metal ions in water are chelated to form water-soluble chelates for easy separation. A chelating agent can be added over several times, if required. A chelating agent is usually used in an aqueous solution. An addition amount of the agent may be determined properly depending on the content of metal ions, such as iron ion, nickel ion and chromium ion, in the reaction mixture. If an amount of a chelating agent added is too small, a coloring prevention effect by the addition of the chelating agent is unsatisfactory. On the other hand, if the agent is added too much, the coloring prevention effect is satisfactory but an excessive amount of the chelating agent may be mixed in the final product of Compound (I) as an impurity. It is therefore favorable to measure a concentration of metal ions contained in the reaction mixture by a known method before the agent is added, and then add an amount of chelating agent corresponding to the concentration of metal ions. An addition amount of a chelating agent is usually from 0.0001 to 0.5 parts by weight, preferably from 0.001 to 0.1 parts by weight, to 100 parts by weight of the reaction mixture.

[0074] The inventions relating to the aforementioned (Composition 7), (Composition 15), (Composition 18), (Composition 24), (Composition 26), (Composition 27), (Composition 28) and (Composition 31) are favorably used as meth-

ods to produce Compound (I) that has a b value of 2.5 or less when measured by a color difference meter or that is visually white. Compound (I) is preferably whiter as a product when used as a developer. Production methods of the prior art have a problem of impossibility to supply such a product stably. The problem is solved with use of the methods of the present invention.

5

Best Forms to Implement the Invention:

[0075] The present invention is described in detail in reference to Examples. The present invention is not limited to the following examples. Compound (II), types of solvents, types of tanks used in the reaction and purification processes and other conditions can be changed at discretion as long as they are not deviated from the points of the invention.

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[0076] Distilled water was used in Reference Example 1, Examples 1 to 3 and Comparative Examples 1 to 4. The content of metal ions in the distilled water, measured by an inductively coupled plasma-atomic emission spectrometer, was 0.05 ppm or less.

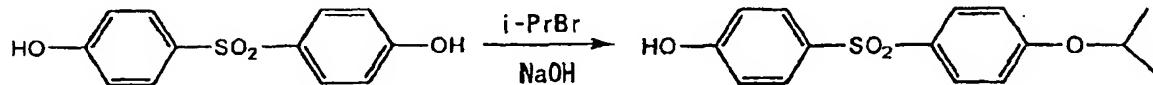
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[0077] In Reference Example 1, Examples 1 to 3 and Comparative Examples 1 to 4, tanks with the inner walls lined with glass (hereinafter referred to as GL tanks) were used as reaction and purification tanks.

Reference Example 1

[0078]

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[0079] 450g of 4,4'-dihydroxydiphenyl sulfone (BPS), 255 ml of a 48% aqueous solution of sodium hydroxide and 120 ml of water were placed in a reaction tank, and mixed with stirring to make the whole solution homogeneous, while 30 temperature rose to 75°C. 225g of isopropyl bromide was slowly dropped into the obtained solution at 55 ± 3°C. The resulting solution was continuously stirred, after the completion of the dropping, at 55 ± 5°C for 20 hours in total from the beginning of the dropping. The obtained reaction solution was used to purify in Example 1 and Comparative Example 1.

35

Example 1: Purification of the mixture containing 4-isopropoxy-4'-hydroxydiphenyl sulfone and impurities [(Composition (1) to (Composition 6)]

[0080] 235 ml of warm water was added to the reaction solution and heated at 80°C for an hour to evaporate unreacted isopropyl bromide to remove. Then, 300 ml of warm water and 250 ml of toluene were added at 80°C to stir sufficiently. 40 The aqueous layer was separated.

(1) First pH adjustment

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[0081] To the obtained aqueous layer were added 1100 ml of toluene and 200 ml of water at 79°C, and stirred at the same temperature for 30 minutes. Further, 30% dilute sulfuric acid was dropped little by little with stirring at 82°C over an hour, to adjust pH of the aqueous layer of the reaction solution uniformly to 8.4 to 8.7. The resulting solution was left to stand at 82°C for 30 minutes and the toluene layer was separated.

50

(2) Second pH adjustment

[0082] To the obtained toluene layer were added 300 ml of toluene and 300 ml of water at 82°C, and 30% dilute sulfuric acid was dropped little by little with stirring at 82°C over an hour, to adjust pH of the aqueous layer uniformly to 8.3 to 8.6. The resulting solution was left to stand at 82°C for 30 minutes and the toluene layer was separated.

55

[0083] To the toluene layer were added 250 ml of toluene and 250 ml of water at 82°C, and stirred at the same temperature for 2 hours. Then, the resulting solution was left to stand at 82°C for 30 minutes and the toluene layer was separated. The obtained toluene layer was cooled to deposit crystals. The crystals were separated by filtration, washed with toluene and dried to give 368.0g of the target compound, 4-isopropoxy-4'-hydroxydiphenyl sulfone, as powder (yield: 70%).

[0084] An analysis of the product for purity by high-performance liquid chromatography showed 99.83% by weight of 4-isopropoxy-4'-hydroxydiphenyl sulfone and 0.01% by weight of BPS.

Comparative Example 1: Purification of the mixture containing 4-isopropoxy-4'-hydroxydiphenyl sulfone and impurities.
[Comparative Example against Example 1]

[0085] 235 ml of warm water was added to the reaction solution obtained in Reference Example 1 and heated at 80°C for an hour to evaporate unreacted isopropyl bromide to remove. Then, 300 ml of warm water and 250 ml of toluene were added at 80°C to stir sufficiently. The aqueous layer was separated.

[0086] To the obtained aqueous layer were added 1100 ml of toluene and 200 ml of water at 79°C, and stirred at the same temperature for 30 minutes. Further, 30% dilute sulfuric acid was dropped little by little with stirring at 82°C over an hour, to adjust pH of the aqueous layer uniformly to 8.4 to 8.7. The resulting solution was left to stand at 82°C for 30 minutes and the toluene layer was separated.

[0087] To the toluene layer were added 250 ml of toluene and 250 ml of water at 82°C, and stirred at the same temperature for 2 hours. Then, the resulting solution was left to stand at 82°C for 30 minutes and the toluene layer was separated.

[0088] The obtained toluene layer was cooled to deposit crystals. The crystals were separated by filtration, washed with toluene and dried to give 368.0g of the target compound, 4-isopropoxy-4'-hydroxydiphenyl sulfone, as powder (yield: 70%).

[0089] An analysis of the product for purity by liquid chromatography showed 98.4% by weight of 4-isopropoxy-4'-hydroxydiphenyl sulfone and 1.5% by weight of BPS.

Example 2 [Example for (Composition 15) to (Composition 17)]

[0090] 450g of 4,4'-dihydroxydiphenyl sulfone (BPS), 255 ml of a 48% aqueous solution of sodium hydroxide and 120 ml of water were placed in a reaction tank and mixed with stirring to make the whole solution homogeneous, while temperature rose to 75°C. 225g of isopropyl bromide was slowly dropped into the obtained solution at 55 ± 3°C. The resulting solution was continuously stirred, after the completion of the dropping, at 55 ± 5°C for 20 hours in total from the beginning of the dropping.

[0091] 235 ml of warm water was added to the reaction solution and heated at 80°C for an hour to evaporate unreacted isopropyl bromide to remove. Then, 300 ml of warm water and 250 ml of toluene were added at 80°C to stir sufficiently. The aqueous layer was separated.

[0092] To the obtained aqueous layer were added 1100 ml of toluene and 200 ml of water at 79°C, and stirred at the same temperature for 30 minutes. The toluene used at this time was toluene recovered from that used for the crystallization of 4-isopropoxy-4'-hydroxydiphenyl sulfone. The content of isopropyl bromide in the toluene layer was 0.5% by weight. Further, 30% dilute sulfuric acid was dropped little by little with stirring at 82°C over an hour, to adjust pH of the aqueous layer of the reaction solution uniformly to 8.4 to 8.7. The resulting solution was left to stand at 82°C for 30 minutes and the toluene layer was separated.

[0093] To the obtained toluene layer were added 300 ml of toluene and 300 ml of water at 82°C, and 30% dilute sulfuric acid was dropped little by little with stirring at 82°C over an hour, to adjust pH of the aqueous layer uniformly to 8.3 to 8.6. The resulting solution was left to stand at 82°C for 30 minutes and the toluene layer was separated.

[0094] To the toluene layer were added 250 ml of toluene and 250 ml of water at 82°C, and stirred at the same temperature for 2 hours. Then, the resulting solution was left to stand at 82°C for 30 minutes and the toluene layer was separated. The obtained toluene layer was cooled to deposit crystals. The crystals were separated by filtration, washed with toluene and dried to give 368.0g of the target compound, 4-isopropoxy-4'-hydroxydiphenyl sulfone, as powder (yield: 70%).

[0095] An analysis of the product for purity by high-performance liquid chromatography showed 99.83% by weight of 4-isopropoxy-4'-hydroxydiphenyl sulfone and 0.01% by weight of BPS. A measurement of the product by a color-difference meter (made by Nippon Denshoku Kogyo Co., Ltd, Model: 1001 DP) showed that the b value was 2.5 or less. No coloring was observed.

Comparative Example 2 [Comparative Example against Example 2]

[0096] Example 2 was repeated, except that recovered toluene was added to adjust pH and the content of isopropyl bromide in the toluene layer was 5.5% by weight, to give 4-isopropoxy-4'-hydroxydiphenyl sulfone with the same yield and purity. The product was however visually colored yellow.

Example 3 [Example for (Composition 7) to (Composition 14)]

[0097] 210g of BPS, 74.2 ml of a 48% aqueous solution of sodium hydroxide and 740 ml of water were placed in a reaction tank, and mixed with stirring to make the whole solution homogeneous, while temperature rose to 80°C. 705 ml of toluene was added to the obtained solution at 70°C and 165g of isopropyl bromide (iPr-Br) was dropped with stirring.

5 ml of toluene was added to the obtained solution at 70°C and 165g of isopropyl bromide (iPr-Br) was dropped with stirring. The resulting solution was stirred at 76 to 80°C for 8 hours. Then, 4.8 ml of a 48% aqueous solution of sodium hydroxide and 22g of isopropyl bromide were added and stirred at 78 to 80°C for 6 hours. Further, 3.3 ml of a 48% aqueous solution of sodium hydroxide and 25g of isopropyl bromide were added and reacted at 78 to 81°C for 8 hours.

[0098] After the reaction was completed, 300 ml of toluene was added to the reaction solution and heated at 80°C

10 for 3 hours to evaporate unreacted isopropyl bromide to remove completely.

[0099] Then, 200 ml of water, 694 ml of toluene, 2.5g of anhydrous sodium carbonate (soda ash) and 10 ml of warm water were added to the reaction solution, and further a 48% aqueous solution of sodium hydroxide was added to adjust pH of the reaction solution to 8.55 ± 0.02. The resulting solution was left to stand for 30 minutes and the toluene layer was separated. To the toluene layer were added 500 ml of water and 800 ml of toluene at 75 to 80°C. The resulting solution was stirred at the same temperature for 30 minutes, and left to stand for 30 minutes. The toluene layer was separated and cooled. The deposited crystals were separated by filtration, washed with water and dried to give 171.7g of the target compound, 4-isopropoxy-4'-hydroxydiphenyl sulfone, as powder (yield: 70%). At this time, an amount of isopropyl bromide contained in the toluene layer was analyzed by gas chromatography, being 0.5% by weight.

[0100] The obtained 4-isopropoxy-4'-hydroxydiphenyl sulfone was 99% or more in purity, and had a b value of 2.5 or less when measured by a color-difference meter (made by Nippon Denshoku Kogyo Co., Ltd, Model: 1001 DP). No coloring was observed.

Example 4 [Example for (Composition 18) to (Composition 23)]

[0101] 450g of BPS, 255 ml of a 48% aqueous solution of sodium hydroxide and 120 ml of water were placed in a reaction tank, and mixed with stirring to make the whole solution homogeneous, while temperature rose to 75°C. 225g of isopropyl bromide was slowly dropped into the obtained solution at 55 ± 3°C. The resulting solution was continuously stirred further at 55 ± 5°C after the dropping was finished.

[0102] The reaction was terminated when 20 hours in total passed since the dropping started. A part of the reaction solution was taken as a sample and analyzed by high-performance liquid chromatography (HPLC). The result showed 67% of 4-isopropoxy-4'-hydroxydiphenyl sulfone, 32% of BPS and 1% of 4,4'-diisopropoxydiphenyl sulfone. The reaction solution was heated at 80°C for an hour to evaporate unreacted isopropyl bromide to remove. Further, 24 ml of warm water (0.05 parts by weight to a part by weight of BPS) was added to the reaction solution and heated at 80°C for an hour, and further 235 ml of warm water was added and heated at 80°C for an hour to evaporate unreacted isopropyl bromide to remove. A part of the reaction solution was taken as a sample and analyzed by HPLC. The result showed 70% of 4-isopropoxy-4'-hydroxydiphenyl sulfone, 29% of BPS, and 1% of 4,4'-diisopropoxydiphenyl sulfone. An increase of a byproduct, 4,4'-diisopropoxydiphenyl sulfone, was not observed. Then, 300 ml of warm water and 250 ml of toluene were added to stir sufficiently and the aqueous layer was separated.

[0103] 1100 ml of toluene and 200 ml of water were added to the aqueous layer at 79°C and stirred at the same temperature for 30 minutes. Further, 30% dilute sulfuric acid was dropped little by little with stirring at 82°C over an hour to adjust pH of the reaction solution uniformly to 8.4 to 8.7. The resulting solution was left to stand at 82°C for 30 minutes and the toluene layer was separated.

[0104] 300 ml of toluene and 300 ml of water were added to the toluene layer at 82°C, and 30% dilute sulfuric acid was dropped little by little with stirring at 82°C over an hour to adjust pH of the whole solution uniformly to 8.3 to 8.6. The resulting solution was left to stand at 82°C for 30 minutes and the toluene layer was separated. Further, 250 ml of toluene and 250 ml of water were added to the toluene layer at 82°C, and stirred at the same temperature for 2 hours. The resulting solution was left to stand at 82°C for 30 minutes and the toluene layer was separated.

[0105] The toluene layer was cooled to 10 to 35°C to deposit crystals. The crystals were separated by filtration, washed with water and dried to give 368.0g of the target compound, 4-isopropoxy-4'-hydroxydiphenyl sulfone, as powder (yield: 70%). At this time, an amount of isopropyl bromide contained in the toluene layer was analyzed by gas chromatography, being 0.8% by weight.

[0106] The obtained powder of 4-isopropoxy-4'-hydroxydiphenyl sulfone was 99% or more in purity, and had a b value of 2.5 or less when measured by a color-difference meter (made by Nippon Denshoku Kogyo Co., Ltd, Model: 1001 DP). No coloring was observed.

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Comparative Example 3 [Comparative Example against Example 3]

[0107] Example 2 was repeated to give 171.7g of 4-isopropoxy-4'-hydroxydiphenyl sulfone as powder (yield: 70%).

except that the process was omitted for removing unreacted isopropyl bromide by adding 300 ml of toluene to the reaction solution to heat at 80°C for 3 hours after the reaction was completed.

[0108] The product was 99% or more in purity and had a b value of 4.4 when measured by a color difference meter (made by Nippon Denshoku Kogyo Co., Ltd, Model: 1001 DP). It was colored light yellow.

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Comparative Example 4 [Comparative Example against Example 4]

[0109] 450g of BPS, 255 ml of a 48% aqueous solution of sodium hydroxide and 120 ml of water were placed in a reaction tank, and mixed with stirring to make the whole solution homogeneous, while temperature rose to 75°C. 225g of isopropyl bromide was slowly dropped into the obtained solution at 55 ± 3°C. The resulting solution was continuously stirred further at 55 ± 5°C after the dropping was finished.

[0110] The reaction was terminated when 20 hours in total passed since the dropping started. A part of the reaction solution was taken as a sample and analyzed by high performance liquid chromatography (HPLC). The result showed 67% of 4-isopropoxy-4'-hydroxydiphenyl sulfone, 32% of BPS, and 1% of 4,4'-disisopropoxydiphenyl sulfone. 235 ml of warm water (0.52 parts by weight to a part by weight of BPS) was added to the reaction solution and heated at 80°C for an hour to evaporate unreacted isopropyl bromide to remove. A part of the reaction solution was taken as a sample and analyzed by HPLC. The result showed 70% of 4-isopropoxy-4'-hydroxydiphenyl sulfone, 26% of BPS, and 4% of 4,4'-disisopropoxydiphenyl sulfone. An increase of a byproduct, 4,4'-disisopropoxydiphenyl sulfone, was observed. Then, 300 ml of warm water and 250 ml of toluene were added at 80°C to stir sufficiently and the aqueous layer was separated.

[0111] 1100 ml of toluene and 200 ml of water were added to the aqueous layer at 79°C and stirred at the same temperature for 30 minutes. Further, 30% dilute sulfuric acid was dropped little by little with stirring at 82°C over an hour to adjust pH of the reaction solution uniformly to 8.4 to 8.7. The resulting solution was left to stand at 82°C for 30 minutes and the toluene layer was separated.

[0112] 300 ml of toluene and 300 ml of water were added to the toluene layer at 82°C, and 30% dilute sulfuric acid was dropped little by little with stirring at 82°C over an hour to adjust pH of the whole solution uniformly to 8.3 to 8.6. The resulting solution was left to stand at 82°C for 30 minutes and the toluene layer was separated. Further, 250 ml of toluene and 250 ml of water were added to the toluene layer at 82°C, and stirred at the same temperature for 2 hours. The resulting solution was left to stand at 82°C for 30 minutes and the toluene layer was separated.

[0113] The toluene layer was cooled to 10 to 35°C to deposit crystals. The crystals were separated by filtration, washed with water and dried to give 368.0g of the target compound, 4-isopropoxy-4'-hydroxydiphenyl sulfone, as powder (yield: 70%). At this time, an amount of isopropyl bromide contained in the toluene layer was analyzed by gas chromatography, being 0.8% by weight.

[0114] The obtained powder of 4-isopropoxy-4'-hydroxydiphenyl sulfone was 99% or more in purity, and had a b value of 2.5 or less when measured by a color-difference meter (made by Nippon Denshoku Kogyo Co., Ltd, Model: 1001 DP). No coloring was observed.

Example 5 [Example for (Composition 24) to (Composition 30)]

[0115] In Example 5 and Reference Example 2, distilled water was used in all occasions. In Comparative Example 5 and Reference Example 3, industrial water was used throughout. The distilled water and industrial water were measured for the contents of iron components by an inductively coupled plasma-atomic emission spectroscope. The former contained 0.05 ppm or less of iron components and the latter 0.26 ppm.

[0116] GL tanks were used as reaction and purification tanks in Example 5 and Reference Example 2, and SUS tanks, which are usually used in the art, in Comparative Example 5 and Reference Example 3.

[0117] 450g of 4,4'-dihydroxydiphenyl sulfone (BPS), 255 ml of a 48% aqueous solution of sodium hydroxide and 120 ml of distilled water were placed in a GL tank, and mixed with stirring to make the whole solution homogeneous, while temperature rose to 75°C. 225g of isopropyl bromide was slowly dropped into the obtained solution at 55 ± 3°C. The resulting solution was continuously stirred further at 55 ± 5°C after the dropping was finished. When 20 hours in total passed since the dropping started, 235 ml of distilled water of 80°C was added to the reaction solution. The resulting solution was heated at 80°C for an hour to evaporate unreacted isopropyl bromide to remove. Then, 300 ml of distilled water of 80°C and 250 ml of toluene were added at 80°C to stir sufficiently and the aqueous layer was separated.

[0118] Then, 1100 ml of toluene and 200 ml of distilled water were added to the aqueous layer at 79°C and stirred at the same temperature for 30 minutes. Further, 30% dilute sulfuric acid was dropped little by little with stirring at 82°C over an hour to adjust pH of the reaction solution uniformly to 8.3 to 8.7. The resulting solution was left to stand at 82°C for 30 minutes and the toluene layer was separated. Further, 250 ml of toluene and 250 ml of water were added to the toluene layer at 82°C, and stirred at the same temperature for 2 hours. The resulting solution was left to stand at 82°C for 30 minutes and the toluene layer was separated.

[0119] The obtained toluene layer was cooled to deposit crystals. The crystals were separated by filtration, washed with water and dried to give 368.0g of the target compound, 4-isopropoxy-4'-hydroxydiphenyl sulfone, as powder (yield: 70%).

[0120] The obtained 4-isopropoxy-4'-hydroxydiphenyl sulfone was 98% or more in purity, and had a ΔE value of 2.5 or less when measured by a color-difference meter (made by Nippon Denshoku Kogyo Co., Ltd, Model: 1001 DP). No coloring was observed.

Comparative Example 5 [Comparative Example against Example 5]

10 [0121] Example 4 was repeated to give 365.0g of 4-isopropoxy-4'-hydroxydiphenyl sulfone as powder (yield: 70%), except that SUS tanks were used instead of the GL tanks and industrial water instead of distilled water.

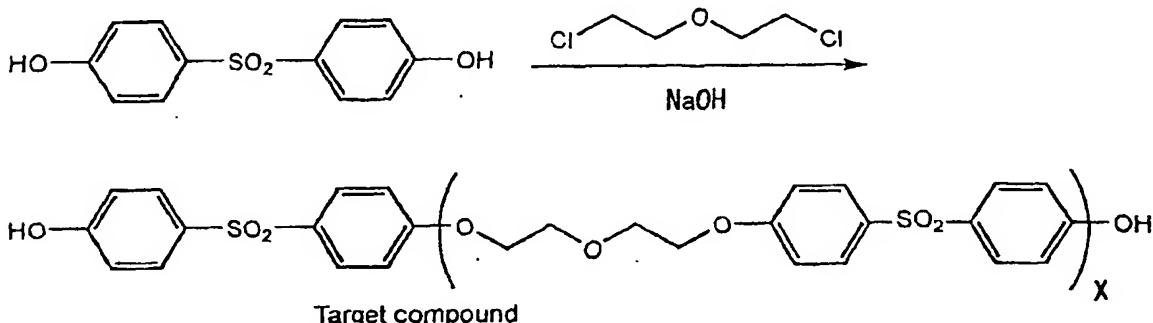
[0122] The obtained 4-isopropoxy-4'-hydroxydiphenyl sulfone was 98% or more in purity, and had a *b* value of 4.1 when measured by a color-difference meter (made by Nippon Denshoku Kogyo Co., Ltd, Model: 1001 DP). It was colored light pink.

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Reference Example 2

[0123]

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35 (Wherein, x is an integer of 1 to 10).

[0124] 47.5 ml of distilled water, 25.6g of sodium hydroxide and 80.0g of 4,4'-dihydroxydiphenyl sulfone were placed in a GL tank, and stirred to dissolve at $110 \pm 2^\circ\text{C}$ for 4 hours. To the resulting solution was added 20.34g of bis(2-chloroethyl) ether at 110 to 112°C and stirred at the same temperature for 8 hours. After the reaction was completed, 108.1 ml of hot water was added to the reaction solution and cooled to 80°C . 167.4 ml of a 90% aqueous methanol solution was added at 70°C and stirred for 30 minutes to make the solution homogeneous. Then, 116.4g of 10% hydrochloric acid was slowly dropped at 71°C to make pH 4 to 5. The resulting solution was left at 71°C for an hour, cooled to 25 to 30°C , and further left for 8 hours. The deposited crystals were separated by filtration, washed with 200 ml of a 50% aqueous methanol solution and dried to give 63.2g of the target compound as powder. Yield: 78%.

[0125] The obtained target compound was 99% or more in purity, and had a b value of 2.5 or less when measured by a color-difference meter (made by Nippon Denshoku Kogyo Co., Ltd, Model: 1001 DP). No coloring was observed.

Reference Example 3

[0126] Reference Example 2 was repeated to give 63.2g of the target compound as powder (yield: 78%), except that SIS tanks were used instead of the GL tanks and industrial water instead of distilled water.

[0127] The obtained target compound was 98% or more in purity, and had a λ value of 4.1 when measured by a color-difference meter (made by Nippon Denshoku Kogyo Co., Ltd, Model: 1001 DP). It was colored light pink.

Example 6 [Example for (Composition 31)]

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[0128] Water used in Examples 6 and 7, Comparative Example 6 and Reference Examples 4 and 5 was industrial water of general use. A measurement by an inductively coupled plasma-atomic emission spectroscope showed that the content of metal ions in the industrial water was 0.1 ppm or more.

[0129] 490g of 4,4'-dihydroxydiphenyl sulfone (BPS), 195ml of a 48% aqueous solution of sodium hydroxide and 120ml of water were placed in an SUS reaction tank, and mixed with stirring to make the whole solution homogeneous, while temperature rose to 76°C. 226g of isopropyl bromide was slowly dropped into the obtained solution at 76°C. The resulting solution was continuously stirred further at 76 to 78°C after the dropping was finished. 235ml of warm water was added to the reaction solution when 20 hours in total passed since the dropping started. The resulting solution was heated at 80°C for an hour to evaporate unreacted isopropyl bromide to remove. Then, 300ml of warm water and 250ml of toluene were added at 80°C to the sufficiently and the aqueous layer was separated.

[0130] Then, 4100ml of toluene and 200ml of water were added to the aqueous layer at 79°C and stirred at the same temperature for 30 minutes. Further, 30% dilute sulfuric acid was dropped little by little with stirring at 82°C over an hour to adjust pH of the reaction solution uniformly to 8.3 to 8.7, and 2.7ml of a 5% aqueous solution of EDTA disodium salt was added. The resulting solution was left to stand at 82°C for 30 minutes and the toluene layer was separated. Further, 250ml of toluene and 250ml of water were added to the toluene layer at 82°C, and stirred at the same temperature for 2 hours. The resulting solution was left to stand at 82°C for 30 minutes and the toluene layer was separated.

[0131] The toluene layer was cooled to deposit crystals. The crystals were separated by filtration, washed with water and dried to give 368.0g of the target compound, 4-isopropoxy-4'-hydroxydiphenyl sulfone, as powder (yield: 70%).

[0132] The obtained 4-isopropoxy-4'-hydroxydiphenyl sulfone was 98% or more in purity, and had a b value of 2.5 or less when measured by a color difference meter (made by Nippon Denshoku Kogyo Co., Ltd, Model: 1001 DP). No coloring was observed.

Example 7 [Example for (Composition 31)]

[0133] 210g of 4,4'-dihydroxydiphenyl sulfone (BPS), 74.2ml of a 48% aqueous solution of sodium hydroxide and 740ml of water were placed in an SUS reaction tank, and mixed with stirring to make the whole solution homogeneous, while temperature rose to 80°C. To the obtained solution was added 705ml of toluene at 70°C, and 169g of isopropyl bromide ($iPrBr$) was slowly dropped. The resulting solution was stirred at 76 to 80°C for 8 hours. Then, 4.8ml of a 48% aqueous solution of sodium hydroxide and 22g of isopropyl bromide were added and stirred at 78 to 80°C for 6 hours. Further, 3.3ml of a 48% aqueous solution of sodium hydroxide and 25g of isopropyl bromide were added and reacted at 78 to 81°C for 8 hours. After the reaction was completed, 300ml of toluene was added to the reaction solution, and heated at 80°C for 3 hours to evaporate unreacted isopropyl bromide to remove completely.

[0134] Then, 200ml of water, 694ml of toluene, 2.5g of anhydrous sodium carbonate (soda ash) and 10ml of warm water were added and further a 48% aqueous solution of sodium hydroxide was added to adjust pH of the reaction solution to 8.55 ± 0.02. To the resulting solution was added 1.2ml of a 5% aqueous solution of EDTA disodium salt and left to stand for 30 minutes. The toluene layer was then separated. 500ml of water and 800ml of toluene were added to the toluene layer at 75 to 80°C, and stirred at the same temperature for 30 minutes. The toluene layer was separated.

[0135] The toluene layer was cooled. The deposited crystals were separated by filtration, washed with water and dried to give 171.7g of the target compound, 4-isopropoxy-4'-hydroxydiphenyl sulfone, as powder (yield: 70%).

[0136] The obtained 4-isopropoxy-4'-hydroxydiphenyl sulfone was 98% or more in purity, and had a b value of 2.5 or less when measured by a color-difference meter (made by Nippon Denshoku Kogyo Co., Ltd, Model: 1001 DP). No coloring was observed.

Comparative Example 6 [Comparative Example against Example 5]

[0137] Example 5 was repeated to give 368.0g of 4-isopropoxy-4'-hydroxydiphenyl sulfone as powder (yield: 70%), except that the operation of adding a 5% aqueous solution of EDTA disodium salt to the reaction solution was omitted in the purification process.

[0138] The obtained 4-isopropoxy-4'-hydroxydiphenyl sulfone was 98% or more in purity, and had a b value of 4.1 when measured by a color-difference meter (made by Nippon Denshoku Kogyo Co., Ltd, Model: 1001 DP). It was colored light yellow.

Reference Example 4: Production of the same target compound as that in Reference Example 2

[0139] In a 500-ml, four-neck flask were placed 47.5ml of water, 25.6g of sodium hydroxide and 80.0g of 4,4'-dihydroxydiphenyl sulfone and stirred to dissolve at $110 \pm 2^\circ\text{C}$ for 4 hours. 20.34g of bis(2-chloroethyl) ether was added to the resulting solution at 110 to 112°C, and stirred at the same temperature for 8 hours. After the reaction was completed, 108.1ml of hot water was added to the reaction solution and cooled to 80°C. 167.4ml of a 90% aqueous-methanol solution was added to the resulting solution and stirred for 30 minutes to make the solution homogeneous.

Then, 0.5 ml of a 5% aqueous solution of EDTA disodium salt was added and 116.4g of 10% hydrochloric acid was slowly dropped at 71°C to adjust pH to 4 to 5. The resulting solution was left at 71°C for an hour, cooled to 25 to 30°C, and further left for 8 hours. The deposited crystals were separated by filtration, washed with 200 ml of a 50% aqueous methanol solution, and dried to give 63.2g of the target compound as powder. Yield: 78%.

5 [0140] The target compound was 99% or more in purity, and had a b value of 2.5 or less when measured by a color-difference meter (made by Nippon Denshoku Kogyo Co., Ltd, Model: 1001 DP). No coloring was observed.

Reference Example 5

10 [0141] Reference Example 4 was repeated to give 63.2g of the target compound as powder (yield: 78%), except that the operation of adding a 5% aqueous solution of EDTA disodium salt to the reaction solution was omitted in the purification process.

[0142] The obtained target compound was 98% or more in purity, and had a b value of 4.1 when measured by a color-difference meter (made by Nippon Denshoku Kogyo Co., Ltd, Model: 1001 DP). It was colored light yellow.

15 Example 7 [Example for (Composition 32) to (Composition 37)]

[0143] 577g of 4-isopropoxy-4'-hydroxydiphenyl sulfone, that was crystallized from toluene and filtrated in the same way as those in Reference Example 1 and Example 1 and not dried yet, formed a molecular compound with toluene, 20 and had the toluene solvent attached in addition to the solvation toluene. The 4-isopropoxy-4'-hydroxydiphenyl sulfone before being dried was heated to dry under reduced pressure with a paddle dryer under the following operation conditions:

25 Pressure reduction degree: 60 to 150 mmHg

Heating temperature: 80 to 85°C

Stirring rate: 2 to 3 revolutions/minute

Drying duration: 16 hours

30 [0144] After the compound was dried, 4-isopropoxy-4'-hydroxydiphenyl sulfone contained 0.1% by weight or less of toluene. No block particles were observed. The product was easily pulverized to fine particles even in the subsequent pulverization process.

Comparative Example 7 [Comparative Example against Example 7]

35 [0145] 4-Isopropoxy-4'-hydroxydiphenyl sulfone of the same conditions as those in Example 7 was heated to dry under the same conditions as those in Example 8, except that a dryer with heating under reduced pressure without a stirring apparatus was used, instead of a paddle dryer. After the compound was dried, there were a large amount of block particles observed. The compound after dried was heavier than that in Example 7. Besides, it took a long time to pulverize the compound to a particle size preset for the product in the subsequent pulverization process.

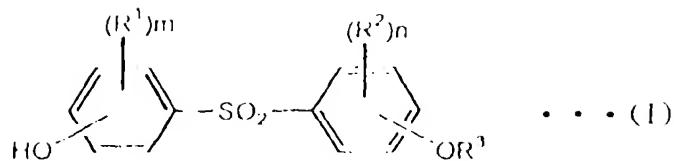
40 Applicability in Industry:

[0146] As described above, the present invention relates to methods for producing 4,4'-dihydroxydiphenyl sulfone monoethers, in which a non-colored, highly pure target compound can be efficiently isolated from a mixture that even 45 contains the target compound and impurities at high concentrations.

[0147] 4,4'-Dihydroxydiphenyl sulfone monoethers are compounds useful as developers. The methods of the present invention stably provide products of high quality, having a high value of use in industry.

50 **Claims**

1. A process for the preparation of a compound represented by Formula (I)



10 (wherein, R¹ and R² are each independently halogen, alkyl having 1 to 8 carbons or alkenyl having 2 to 8 carbons, m and n are each independently 0 or an integer of 1 to 4, and R³ is alkyl having 1 to 8 carbons, alkenyl having 2 to 8 carbons, cycloalkyl having 3 to 8 carbons or optionally substituted aralkyl), in which there are processes that an aqueous solution containing a compound of Formula (I) is adjusted pH to a preset value (P1), extracted with an organic solvent and separated to an organic and an aqueous layers, and that water or water adjusted to a fixed pH value is added to the separated organic layer in order to adjust the pH of the aqueous layer to a preset value (P2) for the separation of the organic layer.

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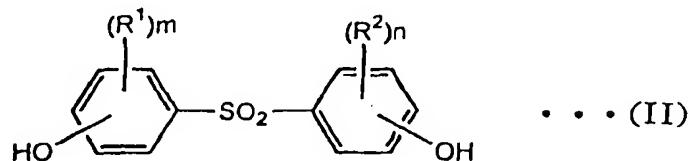
20 2. A process for the preparation of a compound of Formula (I) according to Claim 1 in which the process that an aqueous solution containing a compound of Formula (I) is adjusted pH to a preset value (P1), extracted with an organic solvent and separated to an organic and an aqueous layers is a process that the aqueous layer of a two phase solution consisting of water and a water nonmiscible organic solvent with a mixture containing a compound of Formula (I) is adjusted pH to the preset value (P1) for separating the organic layer.

25 3. A process for the preparation of a compound of Formula (I) according to Claim 1 or 2 in which the said P2 is set to a value different from the said P1.

30 4. A process for the preparation of a compound of Formula (I) according to one of Claims 1 to 3 in which the said P2 is set to a value lower than the said P1.

35 5. A process for the preparation of a compound of Formula (I) according to one of Claims 1 to 4 in which the said P1 is set in a range of 8.4 and 8.7 and the said P2 between 8.3 and 8.6.

40 6. A process for the preparation of a compound of Formula (I) according to one of Claims 1 to 5 in which the aqueous solution containing a compound of Formula (I) is an aqueous solution containing a reaction product obtained from a reaction of a compound represented by Formula (II)



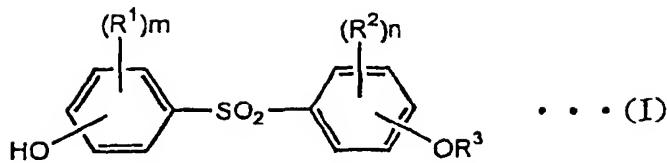
(wherein, R¹ and R² are each independently halogen, alkyl having 1 to 8 carbons or alkenyl having 2 to 8 carbons; m and n are each independently 0 or integer of 1 and 4) with a compound of Formula (III)



(wherein, R³ is alkyl having 1 to 8 carbons, alkenyl having 2 to 8 carbons, cycloalkyl having 3 to 8 carbons or optionally substituted aralkyl, and X is halogen) in a solvent in the presence of a base.

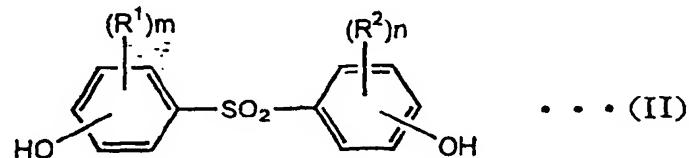
55 7. A process for the preparation of a compound of Formula (I)

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(wherein, R¹ and R² are each independently halogen, alkyl having 1 to 8 carbons or alkenyl having 2 to 8 carbons; m and n are each independently 0 or an integer of 1 to 4; and R³ is alkyl having 1 to 8 carbons, alkenyl having 2 to 8 carbons, cycloalkyl having 3 to 8 carbons or optionally substituted aralkyl), characterized in that, in a method for producing compound of Formula (I) by reacting a compound of Formula (II)

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(wherein, R¹, R², m and n are as defined above) with a compound of Formula (III)

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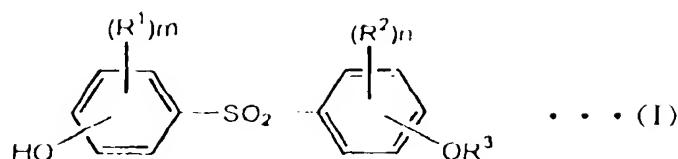


(wherein R³ is as defined above and X is halogen) in a solvent in the presence of a base and the obtained reaction solution is purified, a process is provided that the compound of Formula (III) is removed from the solution produced by the reaction of the compounds of Formulae (II) and (III).

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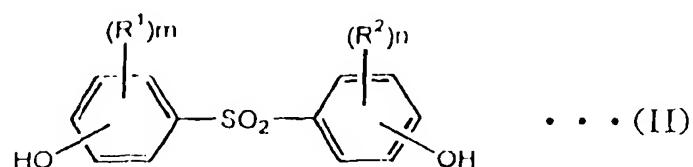
8. A process for the preparation of a compound of Formula (I) according to Claim 7 in which the said reaction solution is the reaction solution after the reaction of compounds of Formulae (II) and (III) is finished.
9. A process for the preparation of a compound of Formula (I) according to Claim 7 or 8 in which the process for removing the compound of Formula (III) from the reaction solution is provided immediately after the compounds of Formulae (II) and (III) are reacted in a solvent in the presence of an alkali.
10. A process for the preparation of a compound of Formula (I) according to one of Claims 7 to 9 in which a process for adjusting pH of solutions including the reaction solution is provided in the production method of a compound of Formula (I), and the process for removing the compound of Formula (III) from the reaction solution is provided immediately before the process for adjusting the pH of the solutions including the reaction solution.
11. A process for the preparation of a compound of Formula (I) according to one of Claims 7 to 10 in which the process for removing the compound of Formula (II) is a process for removing the compound of Formula (III) together with the reaction solvent from the reaction solution by distillation.
12. A process for the preparation of a compound of Formula (I) according to one of Claims 7 to 10 in which the process for removing the compound of Formula (III) is a process for removing the compound together with a mixture of water and a solvent azeotropic with water by distillation.
13. A process for the preparation of a compound of Formula (I) according to one of Claims 7 to 12 in which the reaction solvent is water.
14. A process for the preparation of a compound of Formula (I) according to one of Claims 7 to 13 in which a process for depositing the compound of Formula (I) from an organic solvent as crystals is provided in the production method of the compound of Formula (I), and the compound of Formula (III) is removed so that the concentration of the compound in the organic solvent is 1% by weight or less.

15. A process for the preparation of a compound of Formula (I)



10 (wherein, R¹ and R² are each independently halogen, alkyl having 1 to 8 carbons or alkenyl having 2 to 8 carbons, m and n are each independently 0 or an integer of 1 to 4, and R³ is alkyl having 1 to 8 carbons, alkenyl having 2 to 8 carbons, cycloalkyl having 3 to 8 carbons or optionally substituted aralkyl), characterized in that, in a method for producing a compound of Formula (I) by reacting a compound of Formula (II)

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25 (wherein, R¹, R², m and n are as defined above) with a compound of Formula (III)

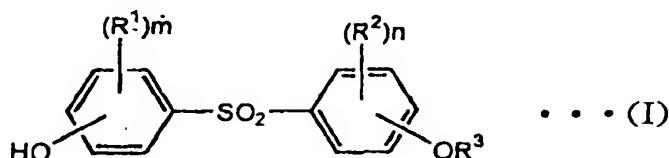


(wherein R³ is as defined above and X is halogen) in a solvent in the presence of a base and the obtained reaction solution is purified, the compound of Formula (III) in the organic solvent is 5% by weight or less in concentration in the process for purifying the reaction mixture of the compounds of Formulae (II) and (III) with water and an organic solvent.

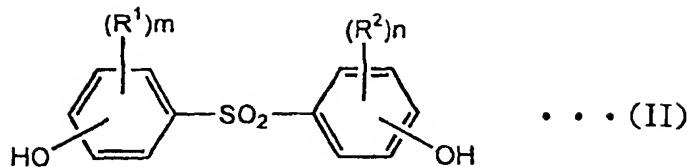
35 16. A process for the preparation of a compound of Formula (I) according to Claim 15 in which the compound of Formula (III) in the organic solvent is 2% by weight or less in concentration.

40 17. A process for the preparation of a compound of Formula (I) according to Claim 15 in which the compound of Formula (III) in the organic solvent is 1% by weight or less in concentration.

45 18. A process for the preparation of a compound of Formula (I)



55 (wherein, R¹ and R² are each independently halogen, alkyl having 1 to 8 carbons or alkenyl having 2 to 8 carbons; m and n are each independently 0 or an integer of 1 to 4; and R³ is alkyl having 1 to 8 carbons, alkenyl having 2 to 8 carbons, cycloalkyl having 3 to 8 carbons or optionally substituted aralkyl), characterized in that, in a method for producing a compound of Formula (I) with a process for reacting a compound of Formula (II)



10 (wherein, R¹, R², m and n are as defined above) with a compound of Formula (III)



15 (wherein R³ is as defined above and X is halogen) in the presence of 1.5 to 3 moles of an alkali to a mole of the compound of Formula (II) in 0.3 to 1.5 parts by weight of an aqueous solvent to a part by weight of the compound of Formula (II) and the compound of Formula (III) is removed by distillation, the compound of Formula (III) is heated to distill out and then water is further added to distill the compound of Formula (III) to remove.

20 19. A process for the preparation of a compound of Formula (I) according to Claim 18 in which an amount of water added is in the range of 0.03 and 0.1 parts by weight to a part by weight of the compound of Formula (II).

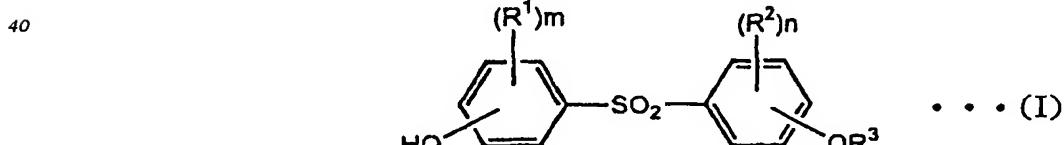
25 20. A process for the preparation of a compound of Formula (I) according to Claim 18 in which an amount of water added is in the range of 0.04 and 0.08 parts by weight to a part by weight of the compound of Formula (II).

21. A process for the preparation of a compound of Formula (I) according to Claim 18 in which water is added separately over two or more times.

30 22. A process for the preparation of a compound of Formula (I) according to Claim 21 in which an amount of water added at the beginning is in the range of 0.03 and 0.1 parts by weight to a part by weight of the compound of Formula (II).

23. A process for the preparation of a compound of Formula (I) according to Claim 21 in which an amount of water added is between 0.04 and 0.08 parts by weight to a part by weight of the compound of Formula (II).

35 24. A process for the preparation of a compound of Formula (I)



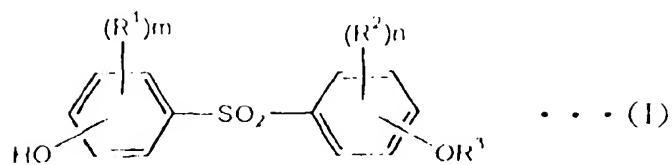
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(wherein, R¹ and R² are each independently halogen, alkyl having 1 to 8 carbons or alkenyl having 2 to 8 carbons; m and n are each independently 0 or an integer of 1 to 4; and R³ is alkyl having 1 to 8 carbons, alkenyl having 2 to 8 carbons, cycloalkyl having 3 to 8 carbons or optionally substituted aralkyl), characterized in that, in a method for producing a compound of Formula (I) that a reaction is carried out in a solvent to give the compound of Formula (I), a solvent containing 0.05 ppm or less of iron components is used as the solvent.

50 25. A process for the preparation of a compound of Formula (I) according to Claim 24 in which the reaction solvent is a reaction solvent containing water.

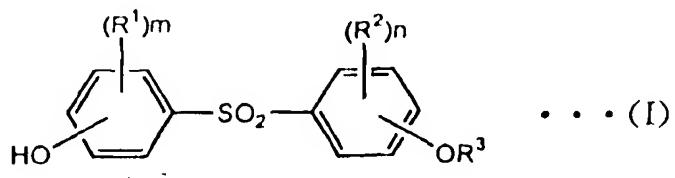
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26. A process for the preparation of a compound of Formula (I)



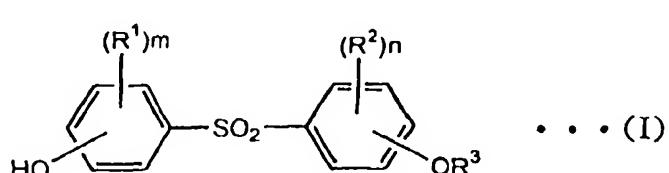
10 (wherein, R¹ and R² are each independently halogen, alkyl having 1 to 8 carbons, or alkenyl having 2 to 8 carbons; m and n are each independently 0 or an integer of 1 to 4; and R³ is alkyl having 1 to 8 carbons, alkenyl having 2 to 8 carbons, cycloalkyl having 3 to 8 carbons or optionally substituted aralkyl), in which water containing 0.05 ppm or less of iron component(s) is used as the water in the purification process for removing compounds, other than the compound of Formula (I), from the mixture containing the compound of Formula (I).

15 27. A process for the preparation of a compound of Formula (I)



25 (wherein, R¹ and R² are each independently halogen, alkyl having 1 to 8 carbons or alkenyl having 2 to 8 carbons; m and n are each independently 0 or an integer of 1 to 4; and R³ is alkyl having 1 to 8 carbons, alkenyl having 2 to 8 carbons, cycloalkyl having 3 to 8 carbons or optionally substituted aralkyl), in which a tank with a corrosion-resistant layer over the inner wall is used in the reaction process for producing the compound of Formula (I).

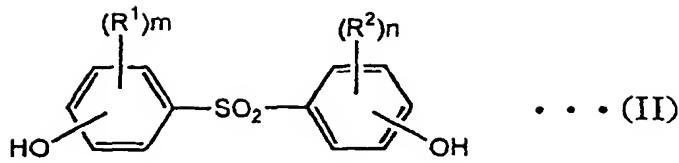
30 28. A process for the preparation of a compound of Formula (I)



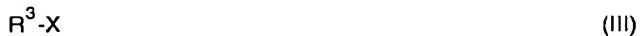
40 (wherein, R¹ and R² are each independently halogen, alkyl having 1 to 8 carbons or alkenyl having 2 to 8 carbons; m and n are each independently 0 or an integer of 1 to 4; and R³ is alkyl having 1 to 8 carbons, alkenyl having 2 to 8 carbons, cycloalkyl having 3 to 8 carbons or optionally substituted aralkyl), in which a tank with a corrosion-resistant layer over the inner wall is used in the purification process for removing compounds, other than the compound of Formula (I), from a mixture containing the compound of Formula (I).

45 29. A process for the preparation of a compound of Formula (I) according to Claim 24 or 25 in which the corrosion-resistant layer is a layer composed of at least one material selected from the group consisting of titanium, glasses and fluorine resins.

50 30. A process for the preparation of a compound of Formula (I) according to one of Claims 24 to 29 in which the reaction process for producing the compound of Formula (I) is a process for reacting a compound represented by Formula (II)

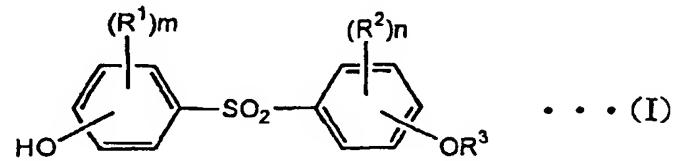


10 (wherein, R¹ and R² are each independently halogen, alkyl having 1 to 8 carbons or alkenyl having 2 to 8 carbons; m and n are each independently 0 or an integer of 1 and 4) with a compound of Formula (III)



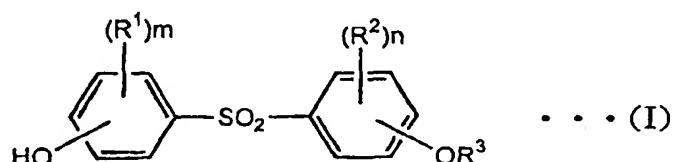
15 (wherein, R³ is as defined above and X is halogen) in a solvent in the presence of a base.

31. A process for the preparation of a compound of Formula (I)



25 (wherein, R¹ and R² are each independently halogen, alkyl having 1 to 8 carbons or alkenyl having 2 to 8 carbons; m and n are each independently 0 or an integer of 1 to 4; and R³ is alkyl having 1 to 8 carbons, alkenyl having 2 to 8 carbons, cycloalkyl having 3 to 8 carbons or optionally substituted aralkyl), in which a chelating agent is added 30 in the purification process for removing compounds, other than the compound of Formula (I), from a mixture containing the compound of Formula (I).

32. A process for the preparation of a compound of Formula (I)



40 (wherein, R¹ and R² are each independently halogen, alkyl having 1 to 8 carbons or alkenyl having 2 to 8 carbons; m and n are each independently 0 or an integer of 1 to 4; and R³ is alkyl having 1 to 8 carbons, alkenyl having 2 to 8 carbons, cycloalkyl having 3 to 8 carbons or optionally substituted aralkyl), characterized in that, in a method 45 for producing the compound of Formula (I) with a drying process, the product is dried with mechanical stir in the drying process.

50 33. A process for the preparation of a compound of Formula (I) according to Claim 32 in which the product is heated to dry under reduced pressure with mechanical stir.

55 34. A process for the preparation of a compound of Formula (I) according to Claim 32 or 33 in which the compound of Formula (I) before drying is in the condition with a property of melting at a temperature below the melting point of the compound of Formula (I).

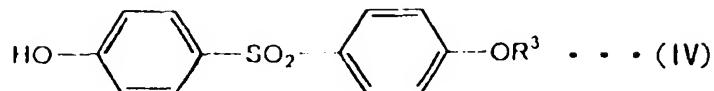
35. A process for the preparation of a compound of Formula (I) according to one of Claims 32 to 34 in which the compound of Formula (I) before drying is in the condition of forming a molecular compound with a solvent.

36. A process for the preparation of a compound of Formula (I) according to Claim 36 in which the solvent is an organic solvent.

37. A process for the preparation of a compound of Formula (I) according to Claim 36 in which the organic solvent is an aromatic hydrocarbon.

38. A process for the preparation of a compound of Formula (I) according to one of Claims 1 to 37 in which the compound of Formula (I) is a compound represented by Formula (IV)

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(wherein, R³ is alkyl having 1 to 8 carbons, alkenyl having 2 to 8 carbons, cycloalkyl having 3 to 8 carbons or optionally substituted aralkyl)

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP02/00410

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl⁷ C07C315/04, 317/22

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl⁷ C07C315/00, 317/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

REGISTRY (STN), CA (STN)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 91/11433 A1 (Yoshitomi Pharmaceutical Industries), 08 August, 1991 (08.08.91), & JP 4-210955 A & US 5284978 A	1-23 24-38
X	JP 3-258760 A (Yoshitomi Pharmaceutical Industries) 19 November, 1991 (19.11.91), Pages 1 to 4 (Family: none)	1-23 24-38
X	JP 60-56949 A (Shinnichi Soka Kogyo Kabushiki Kaisha), 02 April, 1985 (02.04.85), Pages 1 to 4 (Family: none)	1-23 24-38

 Further documents are listed in the continuation of Box C. See patent family annex.

"A"	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E"	earlier document but published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 16 April, 2002 (16.04.02)	Date of mailing of the International search report 14 May, 2002 (14.05.02)
Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer
Facsimile No.	Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP02/00410

(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT	
Category*	Citation of document, with indication, where appropriate, of the relevant passages Relevant to claim No
Y	JP 2001 11001 A (GEA Corp.), 16 January, 2001 (16.01.01), Pages 2, 6, 7 (Family: none)
Y	US 5414149 A (General Electric Co.), 09 May, 1995 (09.05.95), & JP 7-309796 A & EP 670297 A1
Y	JP 11 124362 A (Nippon Soda Co., Ltd.), 11 May, 1999 (11.05.99), Pages 2, 3, 9, 10 (Family: none)

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